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# **Self-organisation of hydrophobic soil and granular surfaces**

Glen McHale<sup>#</sup>, Neil J. Shirtcliffe, Michael I. Newton, F. Brian Pyatt

*School of Biomedical & Natural Sciences, Nottingham Trent University,*

*Clifton Lane, Nottingham NG11 8NS, UK*

Stefan H. Doerr

*Department of Geography, University of Wales, Swansea, Singleton Park,*

*Swansea SA2 8PP, UK*

## **Abstract**

Soil can become extremely water repellent following forest fires or oil spillages, thus preventing penetration of water and increasing run-off and soil erosion. Here the authors show that evaporation of a droplet from the surface of a hydrophobic granular material can be an active process, lifting, self-coating and selectively concentrating small solid grains. Droplet evaporation leads to the formation of temporary liquid marbles and, as droplet volume reduces, particles of different wettability compete for water-air interfacial surface area. This can result in a sorting effect with self-organisation of a mixed hydrophobic-hydrophilic aggregate into a hydrophobic shell surrounding a hydrophilic core.

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#Corresponding author: [glen.mchale@ntu.ac.uk](mailto:glen.mchale@ntu.ac.uk); Tel: +44 115 8483383

Water repellent soil is known to form when a fire volatilizes waxy compounds from the surface litter layer and these waxes subsequently condense on loose, sandy particles within the upper part of the soil profile.<sup>1-4</sup> Industrial spillages and contamination also cause hydrophobic coatings on sand grains, as can microbial action within the soil.<sup>5,6</sup> The hydrophobic coating on soil particles prevents capillary penetration between particles and causes extreme water repellence. The consequences range from localized dry spots on golf courses, which cause grass to die, to severe erosion due to rainsplash, enhanced run-off and the formation of rills.<sup>1-7</sup> One of the simplest and most widely used tests for soil water repellence is the water droplet penetration time test in which a droplet of water is placed on the surface and the time for it to infiltrate into the soil measured.<sup>8</sup> Field scientists have noticed, but rarely commented upon in print, that during such a test the water droplet will often rapidly self-coat in a particulate skin before disappearing. Here we show that this is an active process involving selection and self-organisation of the particles driven by reduction in liquid volume and relative wettability of particles, which has wide applicability to any system involving liquids interacting with granular or powdery surfaces.

To investigate drying of droplets on loose hydrophobic granular surfaces, hydrophobic sand and silica spheres were created and the evaporation sequences for droplets of deionised water studied using video microscopy and a Krüss DSA10 (Drop shape analyser) to obtain contact angles. Experiments were conducted in a closed chamber to prevent air currents. Droplets were carefully dropped onto the sample from a hydrophobised needle of a microsyringe; the needle usually had to be tapped to get the droplet to detach. Beach sand graded to 50-150  $\mu\text{m}$  and spherical silica particles (75  $\mu\text{m}$ , 212-300  $\mu\text{m}$ , 425-600  $\mu\text{m}$  and 710-1180  $\mu\text{m}$ ) were washed in 30% hydrochloric acid (HCl), rinsed with deionised water, dried in a vacuum oven at 80°C and hydrophobised using trimethylsilyl chloride (TMSCl, Aldrich 95%); the sand and silica were subject to a final drying using a vacuum oven at 80°C for three hours. Conclusions

presented in this letter summarise a wide range of experiments and the presented figures are illustrative of the main observations; the specific surfaces used for the data in these figures are described in the relevant sections.

Figure 1 (panels (a)-(d)) shows the successive stages during the evaporation of a droplet of deionised water placed on a hydrophobic sandy surface (TMSCL treated beach sand graded to 50-150  $\mu\text{m}$ ). Initially the droplet sits upon the surface with a few grains of sand attached to the lower part of the droplet, but over time these grains climb ever higher until a complete skin forms and the droplet appears as a liquid marble.<sup>9</sup> Further evaporation causes a buckling of the skin into multi-layers and disordered shapes due to competition between continuing shrinkage and the skin's compressive strength<sup>10,11</sup>, so that the final drying leaves a clump of grains in the centre of a shallow depression (Fig. 1 panel (d)). We reproduced this process with a surface of 75  $\mu\text{m}$  diameter hydrophobic silica spheres (Fig. 1 panels (e)-(h)). Repeating these experiments under saturated vapor conditions within the closed chamber, a skin of grains/spheres did not form. We have also previously shown that droplets do not penetrate into these hydrophobic granular surfaces even when the intrinsic contact angle is substantially less than  $90^\circ$ .<sup>12</sup> We concluded, therefore, that the self-coating process is evaporatively driven.

To test whether the self-coating effect is caused by surface tension gradients, convective flows within the droplet or just by volume change, the extent of coverage was followed during evaporation. If the rise were due to surface tension gradients or evaporatively driven currents the surface area covered by the solid spheres might be expected to increase with time. If the effect is solely a consequence of the loss of surface area as the droplet volume decreases and the incompressibility of the skin of spheres/grains, the area of the droplet surface covered by the skin would be expected to remain constant as the droplet volume decreased. Assuming the droplet is a spherical

cap shape, the surface area of the skin is  $2\pi R h$ , and the product of the height of skin,  $h$ , and the droplet's spherical radius,  $R$ , should remain constant. We confirmed that this was the case quantitatively using experiments with 75  $\mu\text{m}$  diameter hydrophobic silica spheres. After an initial period, this product tended to a constant to within  $\pm 5\%$  before closure of the skin occurred (Fig. 2).

The attachment of a solid grain, initially in air, to the surface of the droplet of water can be understood from the minimisation of surface free energy.<sup>9</sup> If the grain is spherical, then as it attaches it replaces a solid-vapor interfacial area of  $2\pi R_s^2(1+\cos\theta_e)$ , where  $R_s$  is the radius of the grain and  $\theta_e$  is the contact angle, with an equivalent amount of solid-water interfacial area. Simultaneously, the droplet loses water-vapor interfacial area of  $\pi R_s^2 \sin^2\theta_e$ , so that the net change in surface energy is  $\Delta F = 2\pi R_s^2(1+\cos\theta_e)(\gamma_{SL} - \gamma_{SV}) - \pi R_s^2 \sin^2\theta_e \gamma_{LV}$ , where  $\gamma_{ij}$  are the interfacial tensions. Using Young's law this gives

$$\Delta F = -\gamma_{LV} \pi R_s^2 (1 + \cos\theta_e)^2 \quad (1)$$

Equation (1), which is a variation of the Young-Dupré formula, shows the surface energy change is always negative. It is therefore always favourable for spherical solid grains to spontaneously attach to the air-water interface, even if they are hydrophobic.

When a droplet of water is placed on a loose hydrophobic granular surface and left to evaporate freely, the situation is different to evaporation from a hydrophobic surface because the grains forming the surface are not fixed in their positions. Initially, small particles will be peeled from the surface and appear as a coating around the lower part of the droplet as it balls up to minimise its surface area. If droplets of liquids with greater spreading power (or lower surface tension) are used, the initial spreading on the granular surface should be greater and the initial skin more extensive. To test these ideas we gently deposited droplets of undecane, octane, heptane and hexane onto

surfaces composed of fluoro-chemical treated silica particles of diameter 75  $\mu\text{m}$  within the closed chamber equilibrated with vapor of the liquid; this was achieved by placing a wick soaked with the liquid in the container and leaving it sealed for 30 minutes before depositing the droplets. The contact angles of these liquids to the hydrophobic silica surface are  $76^\circ$ ,  $72^\circ$ ,  $67^\circ$  and  $61^\circ$ , respectively, and this systematic change in wettability was mirrored in the initial height of the particulate skin; penetration of these liquids did not occur into these bead packs.<sup>12</sup>

The clump of grains created by deposition, evaporation and buckling of a droplet is not entirely random in its final structure, but involves self-organisation based on relative wettability of the grains. The wettability of each grain determines how much it will protrude from the droplet. Grains which are hydrophobic solid spheres (i.e.  $\theta_e > 90^\circ$ ) have more than half their surface in the air, whilst hydrophilic ones (i.e.  $\theta_e < 90^\circ$ ) have more than half their surface in the water. As the droplet evaporates and the skin begins to close, there will be a competition for air-water interfacial area between attached hydrophilic grains and hydrophobic ones. In this competition, “losing” grains can either be ejected from the interface into air, which would cause an energy change given by the negative of Eq. (1), or be ejected into the interior of the liquid droplet causing an energy change,

$$\Delta F = \gamma_{LV} \pi R_s^2 (1 - \cos \theta_e)^2 \quad (2)$$

For a hydrophilic grain, to move from the interface to the interior always incurs a smaller increase in energy than to be ejected into the air. For a hydrophobic grain, the opposite is true. When two grains of the same size, but different wettabilities, compete for a reducing air-water interface, the one with its contact angle  $\theta_e$  closest to  $90^\circ$  should win and remain at the interface.

To investigate the competition for air-water interfacial area we took transparent silica spheres of diameter 500  $\mu\text{m}$  and blue colored silica spheres of diameter 700  $\mu\text{m}$  possessing contact angles to water of around  $17^\circ$ . We created mixed wettability systems by hydrophobizing the blue hydrophobic spheres with an extreme wash-in solution (Grangers) to obtain a contact angle of  $115^\circ$ . Droplets of deionised water (15  $\mu\text{l}$ ) were then placed on the surfaces formed by these spheres. Drying droplets lifted both hydrophilic and hydrophobic spheres, but the outer skin was composed entirely of the blue hydrophobic ones. On completion of drying we used transparent glue (cyanoacrylate adhesive) to fix the resulting clump of spheres. The internal structure was composed entirely of the (transparent) hydrophilic spheres (Fig. 3). Our two types of spheres differed in size, but according to equations (1) and (2) that difference is an order of magnitude less important than the difference in contact angles. However, to experimentally rule out any dependence on the size and color of these spheres, these experiments were also repeated with the transparent spheres hydrophobized; the same result was observed.

Our measurements show that an apparently simple process of evaporation on a granular or powdery surface involves a self-coating process, which has a selectivity based on the wettability of the grains. This self-coating mechanism explains the qualitative observations noted in field tests of soil water repellence. Moreover, this process can result in the formation of a clump of grains with a hydrophobic shell surrounding a hydrophilic core. These types of wetting and evaporation dependent mechanisms could be responsible for droplets aggregating airborne soot particles<sup>13</sup> and for the surface rich components observed in spray dried powders.<sup>14,15</sup> By design they could be used to self-organise core shell particles and produce Trojans for drug delivery.<sup>16</sup>

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**Author Information** The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to Professor Glen McHale (glen.mchale@ntu.ac.uk).

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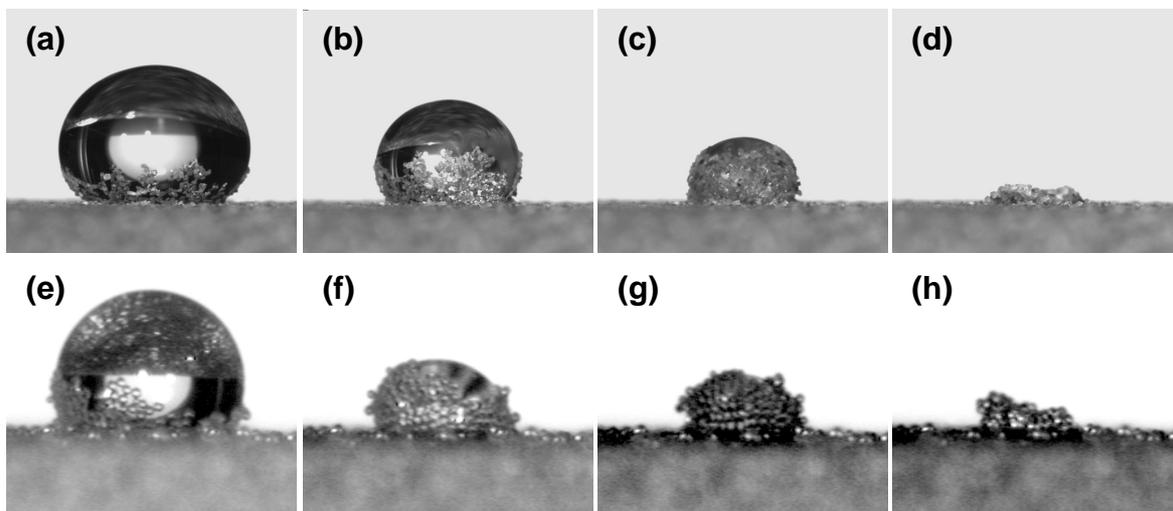
## Figure Captions

**Figure 1** Self coating of an evaporating droplet of water placed on i) hydrophobic sand (panels (a)-(d)), and ii) trimethylsilyl chloride coated silica particles of 75  $\mu\text{m}$  diameter (panels (e)-(h)).

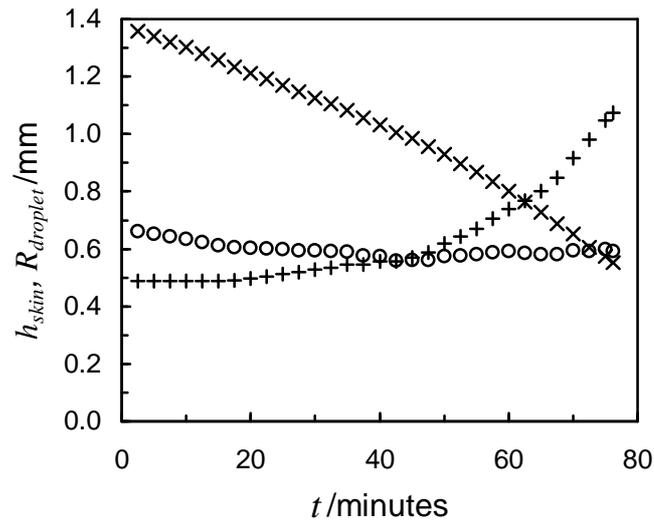
**Figure 2** Evaporation of a water droplet from a bed of 75  $\mu\text{m}$  diameter hydrophobic silica spheres. The plus symbols (+++) show the height of the skin,  $h$ , formed by the spheres, the crosses (xxx) show the droplet spherical radius,  $R$ , and their product is shown by the circles (ooo).

**Figure 3** Aggregate of blue hydrophobic spheres surrounding transparent hydrophilic spheres after the formation of clumps during evaporation.

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