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## **Water-repellent soil and its relationship to granularity, surface roughness and hydrophobicity: a materials science view**

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### **Summary**

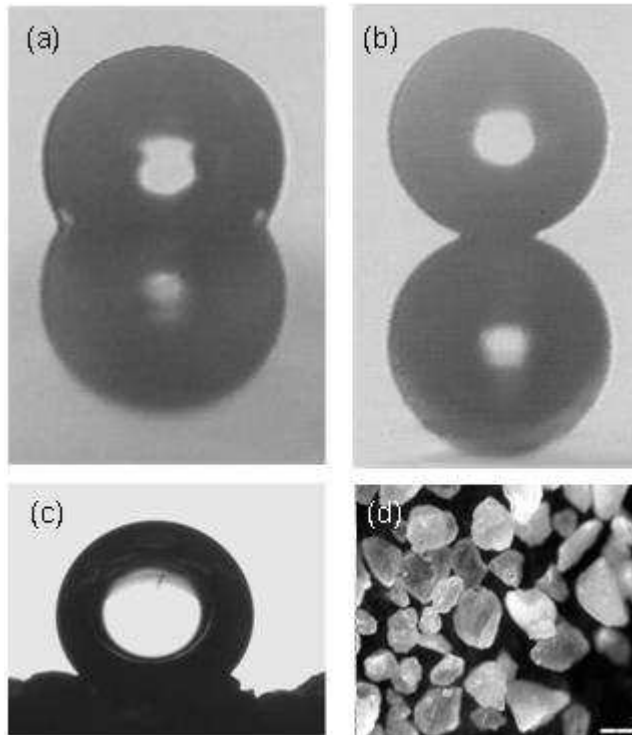
Considerable soil water repellency has been observed at a wide range of locations worldwide. The soil exhibiting water repellency is found within the upper part of the soil profile. The reduced rate of water infiltration into these soils leads to severe run-off erosion, and reduction of plant growth. Soil water repellency is promoted by drying of soil, and can be induced by fire or intense heating of soil containing hydrophobic organic matter. Recent studies outside of soil science have shown how enhancement of the natural water repellency of materials, both porous and granular, by surface texture (i.e. surface roughness, pattern and morphology) into super-hydrophobicity is possible. The similarities between these super-hydrophobic materials and observed properties of water-repellent soil are discussed from a non-soil scientist materials-based perspective. A simple model is developed for a hydrophobic granular surface and it is shown that this can provide a mechanism for enhancement of soil water repellency through the relative size and spacing of grains and pores. The model provides a possible explanation for why soil water repellency should be more prevalent under dry conditions than wet. Consequences for water run-off, raindrop splash and soil erosion are discussed.

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## Introduction

Considerable research has shown that soils can become water repellent through natural processes (DeBano, 2000a; Dekker & Ritsema, 2003) as well as via oil contamination (Roy & McGill, 1998, 2002). Water repellency has been reported for soils around the world under different land uses and climates (De Jonge *et al.*, 1999). Soil that becomes water repellent can present problems due to enhanced run-off and rain-splash causing erosion, and poor water infiltration leading to reduced plant growth (Bisdorn *et al.*, 1993; Terry and Shakesby, 1993; Doerr *et al.*, 2000). The degree of water repellency is related to hydrophobic organic matter with soils of specific types becoming water repellent over a period of time. The water repellent soil is often located close to the surface, i.e. the top few centimetres (Henry & Paul, 1978). The US Fish and Wildlife Service (The Fuel and Fire Effects Monitoring Guide; <http://fire.fws.gov/ifcc/monitor/RefGuide/default.htm>) notes that loose sandy soil is more prone to water repellency and that clay content greater than 5-10% reduces or prevents water repellency (see also Cann, 2000; Karnok & Tucker, 2002; McKissok *et al.*, 2002). Excepting clay, smaller soil-size fractions are believed to lead to higher water repellency (Bisdorn *et al.*, 1993; Doerr *et al.*, 1996), although there are studies indicating coarser texture can lead to greater water repellency (for a discussion see Mataix-Solera & Doerr, 2004). Water-repellent soil is promoted by dry periods. Forest fires or intense heating of soil is known to cause increased water repellency of soil and this is believed to be caused by volatilization of (hydrophobic) waxes from organic matter subsequently condensing and coating soil particles (DeBano, 2000b; Letey, 2001); if temperatures are too high the waxes can be destroyed and the mechanism no longer promotes water repellency. Water-repellent soil can be identified by pooling of water and can be confirmed by water drop penetration time (WDPT) and molarity of ethanol droplet (MED) tests (Moore *et al.*, 1997; Doerr, 1998; Roy & McGill, 2002).

To a non-soil scientist the view arising from the soil science literature is of soil as a convoluted surface consisting of a porous or granular material coated with hydrophobic compounds. The importance of this simplified view of soil, which ignores water repellency caused by hydrophobic micro- or macro-aggregates within soil, is that in recent years enormous steps forward have been made in understanding how hydrophobicity imparted by surface chemistry can be converted into super-hydrophobicity by the surface texture of a material (Blossey, 2003). In a super-hydrophobic material the measured contact angle for a drop of water on the material typically exceeds  $150^\circ$  due to surface roughness or topography enhancing the effect of the surface chemistry. Experiments have also shown the consequences that topographic enhancement of water repellency can have for the interaction of a solid with water and other liquids through the equilibrium shape of droplets on the surface (Onda *et al.*, 1996; Shibuichi *et al.*, 1996) the rolling of droplets (Richard & Quéré, 1999; Miwa *et al.*, 2000) and as impacting droplets (Richard *et al.*, 2002).



**Figure 1** Water drops on (a) a flat copper hydrophobic surface, (b) a textured hydrophobic copper surface, and (c) a hydrophobized sand surface. Panel (d) shows an image of the sand grains in panel (c); scale bar is 200  $\mu\text{m}$  long in two 100  $\mu\text{m}$  sections. Surfaces (a)-(c) have been treated with the same fluorine-based hydrophobic coating.

The dramatic effects of super-hydrophobicity are illustrated in Figures 1. Figure 1(a, b) shows side profiles (and their mirror images) of a small water droplet on a flat hydrophobic surface (Figure 1a) and on a textured surface of the same material (copper) possessing the same surface chemistry (fluorocarbon) (Figure 1b). Figure 1(c) shows a small water droplet on a sand (Aldrich washed sand) hydrophobized using the same chemical treatment as Figure 1(a,b), and Figure 1(d) is a microscope image of the sand grains in Figure 1(c). All the surfaces in Figure 1 were constructed within our laboratory. The hydrophobic effect demonstrated in Figure 1(c), which has a contact angle in excess of  $130^\circ$ , is greater than that reported by Bachmann *et al.* (2000) who hydrophobized laboratory quartz sand.

The developments in understanding super-hydrophobicity have occurred within three usually distinct fields of science: plant science (Neinhuis & Barthlott, 1997; Barthlott *et al.*, 1998; Neinhuis *et al.*, 2001), micro- and nano-materials science (Onda *et al.*, 1996; Shibuichi *et al.*, 1996; Yamauchi *et al.*, 1996; Chen *et al.*, 1999) and physics (Bico *et al.*, 1999; Richard & Quéré, 1999; Herminghaus, 2000; Richard *et al.*, 2002; Quéré *et al.*, 2003), but almost none of this literature has been cited in work on water-repellent soil. The aim of this paper is therefore to present ideas on super-hydrophobic effects and how they may relate to features of water-repellent soil.

## Surface texture and hydrophobic effects

The surface chemistry of a material imparts intrinsic hydrophobicity. Hydrocarbon or fluorocarbon terminated groups provide the greatest levels of water repellency with a water droplet on a smooth PTFE or Teflon<sup>®</sup> surface having a contact angle of around 115-120° (Adamson & Gast, 1997). The contact angle,  $\theta_e$ , is the tangent angle to the liquid surface at the interface with the solid measured from the solid through the liquid (Figure 2a).

No surface chemistry can impart a larger intrinsic contact angle with water than is observed on PTFE, but despite this, water droplets on water repellent soil can show larger contact angles. This is because the observed contact angle on a material is not solely determined by the surface chemistry: a rough or textured surface can promote greater levels of water repellency. Roughness or surface texture, or both, can also lead to partial wetting being converted to wetting, and faster wetting by some liquids (McHale *et al.*, 2004). There are two basic mechanisms that can impart water repellence as assessed by observing droplets of water on the surface.

In the first type of water repellency enhancement, the water contacting the surface follows the profile of the rough surface at all points (Figure 2b) and so the liquid-solid contact area is greater than the plane projection of the area. The ratio of actual area to the planar projection of the area is the roughness factor,  $r$ . In this situation, Wenzel's equation applies (Wenzel, 1936; 1949),

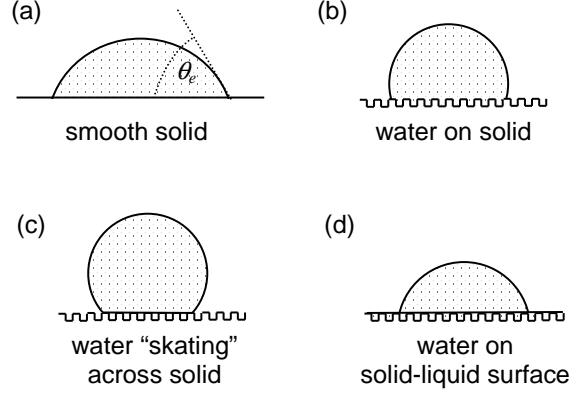
$$\cos \theta_e^W = r \cos \theta_e, \quad (1)$$

where  $\theta_e$  is the surface chemistry determined equilibrium contact angle on a smooth flat surface of the same material and  $\theta_e^W$  is the observed contact angle of the droplet. The intrinsic surface chemistry determined contact angle,  $\theta_e$ , is given by Young's Law,

$$\cos \theta_e = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}, \quad (2)$$

where  $\gamma_{SV}$ ,  $\gamma_{SL}$  and  $\gamma_{LV}$  are the interfacial tensions between the solid-vapor, solid-liquid and the liquid-vapor, respectively (Adamson & Gast, 1997). Since the roughness factor  $r$  is greater than one, the effect of roughness is to enhance the wetting behavior of the surface so that when  $\theta_e > 90^\circ$  the observed contact angle is larger and when  $\theta_e < 90^\circ$  the observed contact angle is smaller. In extreme cases water can completely bead-up on the surface or a non-wetting liquid can become wetting. Using model super-hydrophobic surfaces, this Wenzel form of water repellency has been shown experimentally to occur at slight roughness or texture.

The second type of water-repellency enhancement involves the droplet of water sitting across surface protrusions so that the liquid is effectively supported by a composite of the solid and air beneath the droplet (Figure 2c). When a droplet sits on a chemically heterogeneous surface composed of two materials, type 1 and type 2, possessing two different intrinsic contact angles, the observed contact angle,  $\theta_e^C$ , is then given by the Cassie-Baxter equation (Cassie & Baxter, 1944; Johnson & Dettre, 1964):



**Figure 2** Water drops on surfaces. (a) Definition of contact angle from side profile image of a droplet, (b) Wenzel situation, (c) Cassie-Baxter situation with air gaps, (d) Cassie-Baxter situation with pre-existing water.

$$\cos \theta_e^C = \varphi_1 \cos \theta_1 + (1 - \varphi_1) \cos \theta_2, \quad (3)$$

where  $\varphi_1$  is the fraction of the surface with intrinsic contact angle  $\theta_1$ , due to the material of type 1, and  $(1 - \varphi_1)$  is the fraction of the surface with intrinsic contact angle  $\theta_2$ , due to material of type 2; both  $\theta_1$  and  $\theta_2$  are given by Young's Law, Equation (2). If the first surface is a solid ( $\theta_1 = \theta_e$ ) and the second is air ( $\theta_2 = 180^\circ$ ), the Cassie-Baxter equation gives

$$\cos \theta_V^C = \varphi_s \cos \theta_e - (1 - \varphi_s), \quad (4)$$

where  $\varphi_s$  is the solid surface fraction and a sub-script V has been used to indicate the observed contact angle,  $\theta_V^C$ , which relates to a drop sitting on a composite solid-vapour surface. This equation predicts that contact angles much larger than those due to the surface chemistry alone can be achieved. For example, a wax type surface with  $\theta_e = 110^\circ$  and with a solid surface fraction of 20% gives a much larger observed contact angle of  $\theta_V^C = 150^\circ$ . It is known that this type of surface is created in leaves by a wide range of plants (Neinhuis & Barthlott, 1997; Barthlott *et al.*, 1998; Neinhuis *et al.*, 2001). On most artificially constructed (i.e. model) super-hydrophobic surfaces the Cassie-Baxter effect dominates over the Wenzel form once roughness and/or surface texture or porosity becomes large, although we emphasize that the Wenzel effect can occur with both hydrophobic and hydrophilic surfaces. The Cassie-Baxter state can sometimes be a metastable state rather than the true minimum energy configuration and under those circumstances applying pressure can convert a droplet into a Wenzel state. Whenever the contact angle predicted by Equation (4) is less than that predicted by Equation (1), the Cassie-Baxter state is the true minimum energy equilibrium state. Water droplets grown on a surface by condensation rather than deposited as droplets tend to start in the Wenzel state (Quéré *et al.*, 2003).

One difference between the Wenzel and Cassie-Baxter types of texture enhancement of water repellency is the effect on contact-angle hysteresis and the ease with which a droplet of water may roll on the surface (Miwa *et al.*, 2000; Quéré *et al.*, 2003). The angle observed when contact line motion first occurs induced by adding liquid into a drop is the advancing angle,  $\theta_a$ . The angle observed when contact line motion first occurs induced by removing liquid from a drop is the receding angle,  $\theta_r$ . The difference in these two angles is the contact-angle hysteresis and the force required to cause a droplet to roll from a sloping surface, e.g. by gravity, is the difference in the cosines of the angles (Quéré *et al.*, 2003). In reviewing interfacial effects in soil water retention theory, Bachmann & van der Ploeg (2002) comment that, in general, surface roughness gives rise to contact-angle hysteresis. This statement is both true and false: it is true when the Wenzel form of enhancement occurs, but false when the Cassie-Baxter form arises. The Cassie-Baxter form is known to cause a reduction in contact-angle hysteresis due to the decreased contact with the solid surface caused by the air beneath the droplet. On the Cassie-Baxter type of surface drops rebound easily and drops can be set into a rolling motion with low tilt angles. Quéré *et al.* (2003) refer to the Wenzel form of contact angle enhancement as “sticky” and the Cassie-Baxter form as “slippy”. The leaves of plants have been shown to have the “slippy” property, which it is believed is part of a “self-cleaning in rain” mechanism. As the drops roll off the surface they collect up surface debris and pathogens and so remove them (Neinhuis & Barthlott, 1997; Aussillous & Quéré, 2001).

Whilst we have focused on the two situations that give rise to large observed contact angles it is worth considering a third case which results in a smaller contact angle than  $\theta_e$ . If a droplet sits on a composite solid-liquid surface (Figure 2d), i.e. liquid pre-existing in the gaps between solid grains, then the Cassie-Baxter equation can again be applied, but with  $\theta_2 = 0^\circ$ ,

$$\cos \theta_W^C = \varphi_1 \cos \theta_e + (1 - \varphi_1). \quad (5)$$

In this case, a wax-type surface with  $\theta_e = 110^\circ$  with a solid surface fraction of 20% gives a much smaller observed contact angle of  $\theta_W^C = 43^\circ$ , i.e. the surface partially wets rather than being hydrophobic.

### **Summary of evidence for super-hydrophobic effects in soil**

In our opinion, the literature on water repellent soil has strong evidence of both super-hydrophobic type effects and of the hydrophobic enhancement being of a Cassie-Baxter form. Images of droplets of water on such soils display contact angles greater than those obtainable purely from the surface chemistry and this suggests the surface roughness and/or texture is both involved and influential. It is known that water-repellent soil arises near the surface and may be related to small grains (although the literature has counter opinions on the grain-size effect) coated in wax arising from vegetation. In contrast, one method of producing model, artificial super-

hydrophobic surfaces is by providing a thin, water-repellent coating (typical intrinsic contact angle of  $110\text{-}120^\circ$ ) to small particles forming a surface – these particles can be sub-micron or between  $1\text{-}30\ \mu\text{m}$ . Larger particle sizes might be possible, but the size range up to  $30\ \mu\text{m}$  has definitely been shown to give contact angles larger than  $150^\circ$ , which is the usual definition of super-hydrophobicity. Soil particle sizes therefore appear to contain fractions which would be susceptible to super-hydrophobic effects. It is also known that the leaves of some plants create a surface texture with micron-sized protrusions and coat these with a wax to produce a continually renewable super-hydrophobic surface (Neinhuis *et al.*, 2001). At the same time it is established that forest fires lead to enhancement of soil water repellency due to vapour deposition of the wax from organic material onto soil particles. This is analogous to the process by which super-hydrophobic leaves are reported to renew their wax layer by a steam-distillation type process (Barthlott *et al.*, 1998). The necessary hydrophobic wax needed for super-hydrophobic effects in soil is therefore present in the soil as organic matter and is known, under appropriate circumstances, to coat the soil particles.

One objection to the suggestion that soil can behave as a super-hydrophobic type material could be the fact it is granular and porous rather than providing a textured surface. However, porous super-hydrophobic materials can be created artificially using, for example, the sol-gel process (Tadanaga *et al.*, 1997). We have reported a super-hydrophobic porous foam material which, when heated to remove the hydrophobic terminal groups, completely imbibes water (Shirtcliffe *et al.*, 2003). Treatment with a hydrophobizing solution was shown to re-establish the super-hydrophobic effect. It is therefore clear that a porous or granular material can, under appropriate circumstances for grain and pore size and a hydrophobic surface chemistry, act as a super-hydrophobic surface.

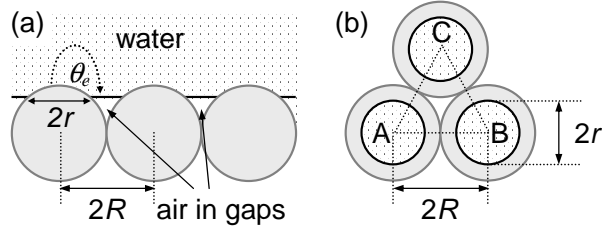
Water repellent soils are more apparent during dry periods and this suggests that the potential for a water droplet to form a liquid-vapor interface in the soil is required. During a dry period a Cassie-Baxter form of water-repellency enhancement with a composite solid-vapour surface, i.e. Equation (4), could be more likely. In contrast, if the soil water content were larger, a Cassie-Baxter form with a composite solid-liquid surface, i.e. Equation (5), could become more likely. The greater the occurrence of the former case, the more water repellency would be observed. This postulated mechanism would also be reversible with local weather and/or seasonal changes as the water content of the soil rose and fell. It has been reported that localized dry spots (LDS) of water-repellent soil occur next to moist soil and that enhanced run-off from these areas occurs. The ease of run-off suggests a Cassie-Baxter, Equation (4), type of super-hydrophobic effect. The disappearance of water repellency of the soil when clay is added, and the more general lack of water repellent clay soils, might also be consistent with a Cassie-Baxter form of super-hydrophobic effect. It is likely that clay both removes the air pores needed for water repellency of the Cassie-Baxter type and promotes wetting. This type of mechanism would not preclude time-dependent changes in hydrophobicity of the surface chemical groups, such as the possible

solvent induced conformational changes of alkyl chains discussed by Roy & McGill (2002).

### A simple model for soil water repellency

In the previous sections we have presented the basic ideas underlying enhancement of water repellency into super-hydrophobicity by texture and have argued that all the ingredients necessary for this to occur will be present in some locations for some soils. In this section, we present a simple model showing how dry soil and wet soil might influence droplets of water on the soil surface. The model is intended to be illustrative of the basic ideas rather than directly applicable to any specific case. It does not include complex grain and pore structures or existence of micro- or macro-aggregates with differing hydrophobicity, or deal with the water flow and transport properties of soil (see e.g. Philip, 1957; Gerke & Köhne, 2002).

Imagine water covering a set of small hydrophobic ( $\theta_e > 90^\circ$ ) solid spheres (particles) of uniform radius,  $R$ , in a close-packed arrangement. The liquid is assumed to contact each sphere with an angle  $\theta_e$ , and then bridge horizontally across the gap to the next sphere (Figure 3a); the horizontal liquid interface bridging between solid spheres is a simplifying approximation. The plan view of this system is shown in Figure 3(b) and the indicated triangle, ABC, can be used to work out the relative fraction of the water surface in contact with the solid spheres; replicating the triangle across the whole system will account for the liquid surface in contact with the spheres. The smaller circles of radius,  $r$ , within each circle of radius,  $R$ , indicate the extent of contact of the water with each sphere.



**Figure 3** (a) Side view of close-packed solid spheres of radius  $R$  with water bridging gaps. (b) Plan view of spheres: triangle ABC enables solid-liquid area to be calculated.

From trigonometry, the solid-liquid area,  $A_{SL}$ , within the triangle ABC in Figure 3(b) is given by

$$A_{SL} = \pi R^2 [1 + \cos \theta_e]. \quad (6)$$

The liquid surface area bridging the gap between the solid spheres,  $A_{LG}$ , is the area of the triangle ABC minus the parts of the smaller circles of radius  $r$ , enclosed by the triangle ABC:

$$A_{LG} = \sqrt{3} R^2 \left[ 1 - \frac{\pi \sin^2 \theta_e}{2\sqrt{3}} \right]. \quad (7)$$

The solid fraction,  $\phi_s$ , needed for the Cassie-Baxter equation is defined as



$$\varphi_s = \frac{A_{SL}}{A_{SL} + A_{LG}}, \quad (8)$$

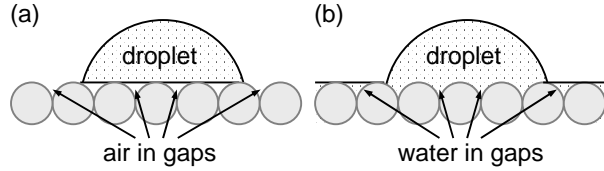
and using Equations (6) and (7) is given by

$$\varphi_s = \frac{1 + \cos \theta_e}{1 + \cos \theta_e + \sqrt{3}/\pi - \frac{1}{2} \sin^2 \theta_e}. \quad (9)$$

A modification to the model is to assume that the spheres are not close-packed, but are separated so that the centre-to-centre separation between spheres is  $2(1+\varepsilon)R$  rather than  $2R$ , where  $R$  remains the radius of the spheres, but a spacing constant,  $\varepsilon$ , has been introduced. This could represent larger soil particles being separated by smaller-sized particles. The fraction of the surface corresponding to the solid-liquid interface,  $\varphi_s(\varepsilon)$ , would then decrease to

$$\varphi_s(\varepsilon) = \frac{1 + \cos \theta_e}{1 + \cos \theta_e + \sqrt{3}(1 + \varepsilon)^2/\pi - \frac{1}{2} \sin^2 \theta_e}. \quad (10)$$

If the gaps between the spheres in the model are assumed to be air (Figure 4a), corresponding to initially dry soil, then Equation (9) can be used in Equation (4) to estimate the observed contact angle according to Cassie-Baxter. The solid fraction given by Equation (9) will be a slight underestimate due to the assumption used in Equation (7) that the liquid interface is horizontal. It is likely that  $\theta_e < 90^\circ$  will also give rise to contact angle enhancement once this assumption is relaxed. Whilst Equations (9) and (10) have no explicit dependence on the size of the solid spheres, they do have an implicit requirement that  $R$  be small enough for the gap between the spheres to be bridged by the liquid under the force of surface tension. The length scale that determines this is the capillary length  $\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2}$ , where  $\rho$  is the density of water and  $g = 9.81 \text{ m s}^{-2}$  is the acceleration due to gravity. For water,  $\kappa^{-1} \approx 2.7 \text{ mm}$  and so requiring sizes to be less than a tenth of the capillary length means the formulae are only likely to be valid for particles in a size range up to a maximum  $\sim 200\text{-}300 \text{ }\mu\text{m}$ .

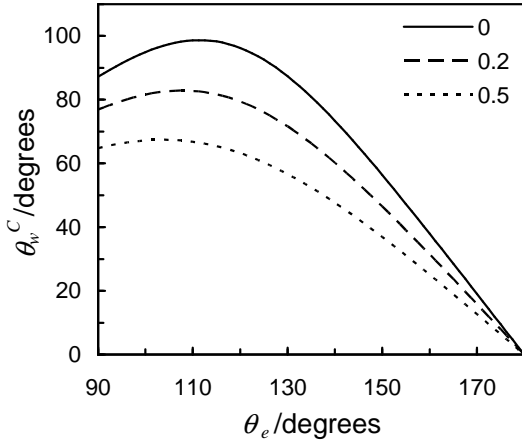


**Figure 4** Side view of close-packed solid spheres with water droplet (a) bridging air gaps, and (b) sitting on a pre-existing layer of water.

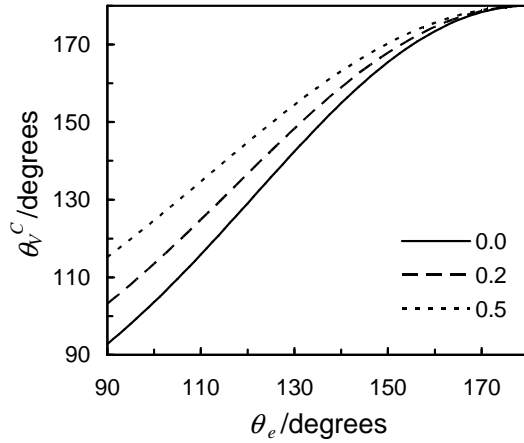
If the gaps between solid spheres are assumed to be filled with water (Figure 4b), corresponding to initially wet soil, then Equation (9) can be used in Equation (5) to estimate the observed contact angle according to Cassie-Baxter. This initial situation, as indicated schematically in Figure 4(b), would require a meniscus at the water-solid interface in order to satisfy the local contact angle relation given by Young's Law, Equation (2). The air-gap case (Figure 4a) would generate a "slippy" surface from which water drops would easily roll (and erode loose material) and from which rainsplash would occur, whereas the liquid-gap case (Figure 4b) would generate a "sticky" surface due to the contact with the pre-existing water.

## Results and discussion

Figure 5 shows the predicted increase in the observed water contact angle,  $\theta_V^C$ , as the intrinsic hydrophobicity, as indicated by the contact angle  $\theta_e$ , increases, i.e. Equation (10) in Equation (4). For close-packed particles the effect is modest, with a  $6^\circ$  increase for a wax-type  $\theta_e = 110^\circ$ . However, the effect becomes stronger as the particles are spaced further apart with  $\varepsilon = 0.2$  giving  $\theta_V^C = 125^\circ$  and  $\varepsilon = 0.5$  giving  $\theta_V^C = 135^\circ$ . For a hydrophobic coating giving  $\theta_e = 115^\circ$  these angles increase to  $\theta_V^C = 131^\circ$  and  $\theta_V^C = 140^\circ$ . The effect of replacing the air gaps with pre-existing water is shown in Figure 6, i.e. Equation (10) in Equation (5). In this case, a reduction in observed contact angle occurs with  $\theta_e = 110^\circ$  resulting in angles of  $\theta_W^C = 99^\circ$ ,  $83^\circ$  and  $67^\circ$  for  $\varepsilon = 0, 0.2$  and  $0.5$ , respectively. However, it is not clear whether the pre-existing water would fill the gaps up to the level assumed by Figure 4(b) and care is therefore needed not to over-interpret Figure 6.



**Figure 5** Predicted and observed contact-angles on a model surface of small spheres with intrinsic hydrophobic contact angles of  $\theta_e > 90^\circ$  and initially possessing air gaps between spheres. The curves  $\varepsilon = 0, 0.2$  and  $0.5$  show the effect of the spacing between spheres ( $\varepsilon = 0$  represents close-packing).



**Figure 6** Predicted and observed contact-angles on a model surface of small spheres with intrinsic hydrophobic contact angles of  $\theta_e > 90^\circ$  and initially possessing water in the gaps between spheres. The curves  $\varepsilon = 0, 0.2$  and  $0.5$  show the effect of the spacing between spheres ( $\varepsilon = 0$  represents close-packing).

Whilst the model with air gaps represents genuine enhancement of water repellency, it does not provide truly super-hydrophobic contact angles  $> 150^\circ$  unless  $\varepsilon > 1$ . This separation of the particles upon which a droplet sits could be possible for a soil with particles of different sizes as a water droplet could be suspended on the largest particles and span across several particles of smaller size without touching them. This type of effect would be consistent with reports of soil-water repellency in fluffy and loose soil. The model also ignores any sharp projections or edges on particles and this is known to be a strong influence leading to super-hydrophobicity; Figure 1(d) shows that sharp projections can be a very strong feature and so the simple model may well underestimate the extent to which granularity can enhance water repellency. When the liquid meets a sharp projection, the tangent for the solid-liquid interface has many possible values and locally satisfying Young's Law, Equation (2), is more straightforward. Suspending the liquid across the gap between

particles then occurs before the solid surface area implied by Equation (6) is achieved and this reduces  $\phi_s$ , resulting in larger observed angles. Moreover, the illustrative system in Figure 1(d) involves relatively large grains and we would expect, on the basis of the model presented, that reducing the grain size or including a fine, hydrophobic fraction would result in contact angles for water approaching or exceeding  $150^\circ$ . Another possible effect is the microstructure of the wax on the surface of the particles. If this microstructure is rough or needle-like due, for example, to the condensation process of volatilized waxes, the solid surface fraction can again be dramatically reduced. This effect has been shown to give contact-angles  $> 170^\circ$  using the paper-sizing agent alkyldiketene dimer (AKD) crystallized under suitable conditions onto a flat surface (Onda *et al.*, 1996). It is also believed that needle-type wax formation can occur on certain leaves, again giving almost unmeasurably large contact angles (Barthlott *et al.*, 1998; Neinhuis *et al.*, 2001). We have also shown experimentally that combining a low aspect-ratio surface texture with a slight roughness can provide a much larger enhancement of hydrophobicity than either the surface texture or roughness alone would provide (Shirtcliffe *et al.*, 2004). It seems probable therefore that the model using uniformly sized spheres underestimates the potential water repellency that soil surface texture can provide. However, this model does show how a basic form of contact-angle enhancement could occur and why this should depend on whether the soil state was previously wet or dry.

If the water-repellent soil is being formed in the Cassie-Baxter manner, as we have suggested, then the work by Richard *et al.* (2002) on how droplets bounce on such surfaces and how droplets rolling on such surfaces can pick up loose material (Richard & Quéré, 1999; Aussillous & Quéré, 2001), even when the loose material is hydrophobic, will have direct relevance to rainsplash and soil erosion. There are also potential implications for how soil-water repellency might be relieved using hydrostatic pressure to force a conversion from the Cassie-Baxter state to the Wenzel state and how maintaining a minimum wetting condition in soil may prevent water-repellent soil reforming. The difference between a metastable Cassie-Baxter state and the Wenzel state and whether a drop is formed by condensation or by deposition could be relevant to issues of water repellency and relative humidity. In the regime where the Wenzel state is the minimum energy state, but a metastable Cassie-Baxter state is possible, a drop formed through condensation might adopt the Wenzel form whilst a deposited drop might adopt the metastable Cassie-Baxter state. More speculatively, there might be a relationship to how landslides could develop based upon a “slippy” layer developing at an interface between two soil types, e.g. clay and a hydrophobic soil. The Cassie-Baxter interpretation for water-repellent soil also suggests that experiments focusing on soil particle sizes and mixtures of soil sizes will be important and that efforts should be made to obtain contact angle measurements and tilt angles for drop run-off or drop contact angle hysteresis measurements. One consequence of the Cassie-Baxter interpretation over the Wenzel interpretation is that the currently favoured experimental methods of water droplet penetration time (WDPT) and molarity of ethanol droplet (MED) tests need to be considered carefully for consistency. Indeed, the need to consider the consistency of these tests is further emphasized by the fact that roughness and/or surface texture can also lead to partial

wetting being converted to wetting, and to faster wetting by some liquids (McHale *et al.*, 2004).

## Conclusion

The causes and effects of soil water repellency have been considered based upon ideas developed to describe super-hydrophobic surfaces. Features observed for water repellent soils that indicate a super-hydrophobic effect has been identified and it has been suggested that a Cassie-Baxter form with occluded air might be occurring. The focus has been upon soil particle size and surface texture enhancement of the hydrophobicity imparted by hydrophobic organic matter. A simple illustrative model has been developed showing the importance of soil surface texture and the pre-existing state of dryness or wetness of the soil.

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## References

- Adamson, A.W. & Gast, A.P. 1997. *Physical Chemistry of Surfaces*. John Wiley & Sons, New York.
- Aussillous, P. & Quéré, D. 2001. Liquid marbles. *Nature*, **411**, 924-927.
- Bachmann, J. & van der Ploeg, R.R. 2002. A review on recent developments in soil water retention theory: interfacial tension and temperature effects. *Journal of Plant Nutrition and Soil Science*, **165**, 468-478.
- Bachmann, J., Ellies, A. & Hartge, K.H. 2000. Development and application of a new sessile drop contact angle method to assess soil water repellency. *Journal of Hydrology*, **231**, 66-75.
- Barthlott, W., Neinhuis, C., Cutler, D., Ditsch, F., Meusel, I., Theisen, I. & Wilhelm, H. 1998. Classification and terminology of plant epicuticular waxes. *Botanical Journal of the Linnean Society*, **126**, 237-260.
- Bico, J., Marzolin, C. & Quéré, D. 1999. Pearl drops. *Europhysics Letters*, **47**, 220-226.
- Bisdom, E.B.A., Dekker, L.W. & Schoute, J.F.T. 1993. Water repellency of sieve fractions from sandy soils and relationships with organic material and soil structure. *Geoderma*, **56**, 105-118.
- Blossey, R. 2003. Self-cleaning surfaces - virtual realities. *Nature Materials*, **2**, 301-306.
- Cann, M.A. 2000. Clay spreading on water repellent sands in the south east of South Australia - promoting sustainable agriculture. *Journal of Hydrology*, **231**, 333-341.
- Cassie, A. B. D. & Baxter S. 1944. Wettability of porous surfaces. *Transactions of the Faraday Society*, **40**, 546-551.
- Chen, W., Fadeev, A.Y., Hsieh, M.C., Oner, D., Youngblood, J. & McCarthy, T.J. 1999. Ultrahydrophobic and ultralyophobic surfaces: some comments and examples. *Langmuir*, **15**, 3395-3399.
- De Jonge, L.W., Jacobsen, O.H. & Møldrup, P. 1999. Soil water repellency: Effects of water content, temperature, and particle size. *Soil Science Society of America Journal*, **63**, 437-442.
- DeBano, L.F. 2000a. Water repellency in soils: a historical overview. *Journal of Hydrology*, **231**, 4-32.
- DeBano, L.F. 2000b. The role of fire and soil heating on water repellency in wildland environments: a review. *Journal of Hydrology*, **231**, 195-206.
- Dekker, L.W. & Ritsema, C.J. (Eds). 2003. *Soil water repellency: Origin, Consequences and Amelioration*, Elsevier, Amsterdam.
- Doerr, S.H. 1998. On standardizing the 'water drop penetration time' and the 'molarity of an ethanol droplet' techniques to classify soil hydrophobicity: A case study using medium textured soils. *Earth Surface Processes and Landforms*, **23**, 663-668.
- Doerr, S.H., Shakesby, R.A. & Walsh, R.P.D. 1996. Soil hydrophobicity variations with depth and particle size fraction in burned and unburned Eucalyptus globulus and Pinus pinaster forest terrain in the Agueda basin, Portugal. *Catena*, **27**, 25-47.

- Doerr, S.H., Shakesby, R.A. & Walsh, R.P.D. 2000. Soil water repellency: its causes, characteristics and hydro-geomorphological significance. *Earth Science Reviews*, **51**, 33-65.
- Gerke, H.H. & Köhne, J.M. 2002. Estimating hydraulic properties of soil aggregate skins from sorptivity and water retention. *Soil Science Society of America Journal*, **66**, 26-36.
- Henry, J.M. & Paul, J.L. 1978. Hydrophobic soils on putting greens. *California Turfgrass Culture*, **28**, 9-11.
- Herminghaus, S. 2000. Roughness-induced non-wetting. *Europhysics Letters*, **52**, 165-170.
- Johnson, R.E. & Dettre, R.H. 1964. Study of an idealized rough surface, in "Contact angle, Wettability and Adhesion". *Advances in Chemistry Series*, **43**, 112-135.
- Karnok, K. & Tucker, K. 2002. Water-repellent soils, Part I. Where are we now? *Golf Course Management*, **70**, 59-62.
- Letey, J. 2001. Causes and consequences of fire-induced soil water repellency. *Hydrological Processes*, **15**, 2867-2875.
- Mataix-Solera, J. & Doerr, S.H. 2004. Hydrophobicity and aggregate stability in calcareous topsoils from fire-affected pine forests in south-eastern Spain. *Geoderma*, **118**, 77-88.
- McHale, G., Shirtcliffe, N.J., Aqil, S., Perry, C.C. & Newton, M.I. 2004. Topography driven spreading. *Physical Review Letters*, **93**, article 036102.
- McKissock, I., Gilkes R.J. & Walker, E.L. 2002. The reduction of water repellency by added clay is influenced by clay and soil properties, *Applied Clay Science*, **20**, 225-241.
- Miwa, M., Nakajima, A., Fujishima, A., Hashimoto, K. & Watanabe, T. 2000. Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces. *Langmuir*, **16**, 5754-5760.
- Moore, G., Blackwell, P. & Carter, D. 1997. Assessing water repellence, *Farmnote 110/96*, Department of Agriculture, Western Australia.
- Neinhuis, C. & Barthlott, W. 1997. Characterization and distribution of water-repellent, self-cleaning plant surfaces. *Annals of Botany*, **79**, 667-677.
- Neinhuis, C., Koch, K. & Barthlott, W. 2001. Movement and regeneration of epicuticular waxes through plant cuticles. *Planta*, **213**, 427-434.
- Onda, T., Shibuichi, S., Satoh, N. & Tsujii, K. 1996. Super-water-repellent fractal surfaces. *Langmuir*, **12**, 2125-2127.
- Philip, J.R. 1957. The theory of infiltration 1. The infiltration equation and its solution. *Soil Science*, **83**, 345-357.
- Quéré, D., Lafuma, A. & Bico, J. 2003. Slippery and sticky microtextured solids. *Nanotechnology*, **14**, 1109-1112.
- Richard, D. & Quéré, D. 1999. Viscous drops rolling on a tilted non-wettable solid. *Europhysics Letters*, **48**, 286-291.
- Richard, D., Clanet, C. & Quéré, D. 2002. Surface phenomena – contact time of a bouncing drop. *Nature*, **417**, 811.
- Roy, J.L. & McGill, W.B. 1998. Characterization of disaggregated nonwettable surface soils found at old crude oil spill sites. *Canadian Journal of Soil Science*, **78**, 331-344.
- Roy, J.L. & McGill, W.B. 2002. Assessing soil water repellency using the molarity of ethanol droplet (MED) test. *Soil Science*, **167**, 83-97.
- Shibuichi, S., Onda, T., Satoh, N. & Tsujii, K. 1996. Super water-repellent surfaces resulting from fractal structure. *Journal of Physical Chemistry*, **100**, 19512-19517.
- Shirtcliffe, N.J., McHale, G., Newton, M.I. & Perry, C.C. 2003. Intrinsically super-hydrophobic organo-silica sol-gel foams. *Langmuir*, **19**, 5626-5631.
- Shirtcliffe, N.J., McHale, G., Newton, M.I., Chabrol, G. & Perry, C.C. 2004. Water repellent surface by dual scale roughness, *Adv. Mater.*, **16**, 1929-1932.
- Tadanaga, K., Katata, N. & Minami, T. 1997. Super-water-repellent Al<sub>2</sub>O<sub>3</sub> coating films with high transparency. *Journal of the American Ceramic Society*, **80**, 1040-1042.
- Terry, J.P. & Shakesby, R.A. 1993. Soil hydrophobicity effects on rainsplash - simulated rainfall and photographic evidence. *Earth Surface Processes and Landforms*, **18**, 519-525.
- Wenzel R.N. 1936. Resistance of solid surfaces to wetting by water. *Industrial and Engineering Chemistry*, **28**, 988-994.
- Wenzel, R.N. 1949. Surface roughness and contact angle. *Journal of Physical and Colloid Chemistry*, **53**, 1466-1467.
- Yamauchi, G., Miller, J.D., Saito, H., Takai, K., Ueda, T., Takazawa, H., Yamamoto, H. & Nislihi, S. 1996. The wetting characteristics of newly developed water-repellent material. *Colloids and Surfaces A*, **116**, 125-134.