Superhydrophobic Sand Repels Water

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A key concept in current fluid dynamics and its applications to biology and technology is a phenomenon known as wetting. Wetting is familiar from everyday life and is simply the ability of a liquid to stay in contact with a solid surface. The wettability depends on the properties of the liquid and the solid and can be characterized by the static equilibrium contact angle θ (the angle at which the liquid-gas interface meets the liquid-solid interface). A contact angle below 90° indicates favourable wetting such that a drop of the liquid would spread over a large amount of the flat solid surface, whereas a high contact angle indicates that very little of the solid is wetted (this can be seen in Figure 1, which shows various stages of surface wetting in terms of the equilibrium contact angle). Nevertheless, this theory generally sounds quite dry or difficult to visualise when explained to students for the first time. The theory of the contact angle also contains some controversies and has undergone some recent developments [1]. We propose a simple classroom demonstration with superhydrophobic sand which gives a concrete visualisation of "superhydrophobicity" and outline how the phenomenon can be explained macroscopically with wetting theory. There are several interesting physical effects which are due to superhydrophobicity: experimental studies have found, for example, that superhydrophobic spheres always splash when they impact on a body of liquid, even at low speeds [2]. In terms of applications, there are various possibilities for water storage with superhydrophobic sand outlined in the chemistry literature [3, 4].

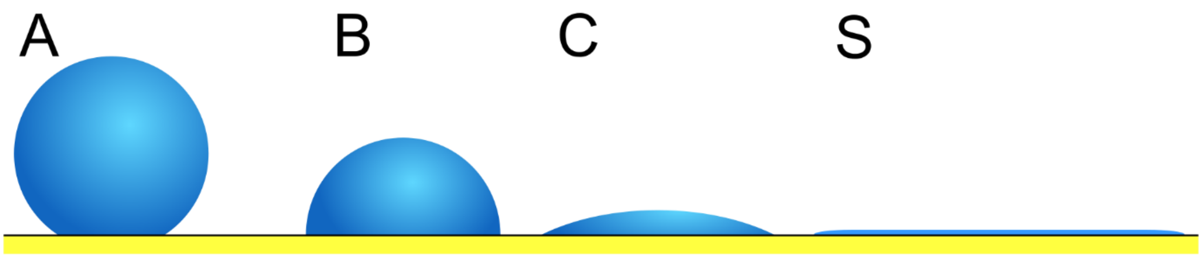

Fig. 1: Droplet A has a large contact angle with the surface (corresponding to little wetting) and droplet S has a very small contact angle (corresponding to favourable wetting) [5]. Accessed from [6].

In Figure 2, we show the classroom demonstration which we have in mind (this should be fascinating for those students who have never seen the phenomenon before). There are some existing Youtube videos which do an excellent job of demonstrating the behaviour of superhydrophobic sand in water [7]. Teachers may note that the sand can be purchased cheaply online by the name of magic sand [8]. In fact, the trick of lifting dry hydrophobic sand from water has been done for many years in stage magic shows, where it is sometimes referred to as the "Sands of the Nile" trick. When the superhydrophobic sand is under the water, it looks to be "wet" and can be manipulated like the usual wet sand which is used to make sand castles. However, as soon as some of the sand is lifted out of the water, it instantly becomes dry. It then clumps up and becomes wet sand again as soon as it is dropped back into the water.

Fig. 2: Demonstration of the wetting properties of superhydrophobic sand.

Students might like to think of other physical phenomena which they have observed which relate to this effect. Certain leaves such as the lotus leaf are hydrophobic and water droplets are repelled away from the surface of the leaf after heavy rain, preventing it from becoming soaked. This principle is mimicked in the design of hydrophobic clothing. Another famous example is the failure of oil to mix with water, which is sometimes attributed to oil being hydrophobic (although the full picture is slightly more complicated) [9].

The full theory behind hydrophobicity is somewhat complicated and involves intermolecular interactions between the solid and the liquid [10, 11]. However, as mentioned before, we can give a simple macroscopic explanation by relying on the concept of the contact angle. Roughly speaking, if a droplet of liquid spreads easily over a flat solid surface, then the adhesive forces involved in the intermolecular interactions are stronger than the cohesive forces (that is to say, it is chemically favourable for surfaces composed of different particles to stick together). If a droplet has difficulty spreading, then the cohesive forces are stronger (that is to say, it is chemically favourable for molecules of the same type to stay together). In both cases, the favourability for wetting is characterised by the static contact angle via the Young equation (or some modification of this equation) after rearranging for $\cos\theta_C$. The most basic possible version of the Young equation is as follows:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG}\cos\theta_C = 0,$$

where θ_C is the contact angle in equilibrium, γ_{LG} is the surface tension, γ_{SG} is the solid-gas interfacial tension and γ_{SL} is the solid-liquid interfacial tension.

The Young equation is not one which will be familiar to most high school students so we attempt to demystify this equation by showing in Figure 3 a diagram of a liquid droplet on a flat solid surface with the above quantities labelled. This diagram should hopefully clarify what the static equilibrium contact angle θ_C represents and the fact that the Young relation is essentially just the net force relation which one obtains by considering Figure 2 and the three different forces of surface tension which are involved in the balance of forces to keep the droplet in static equilibrium. From classical mechanics, students should be familiar with the concept that the net forces all need to add up to zero in order to have a system in static equilibrium. They could also compare to similar mechanical set-ups involving several different tensions in an equilibrium system of ropes and pulleys.

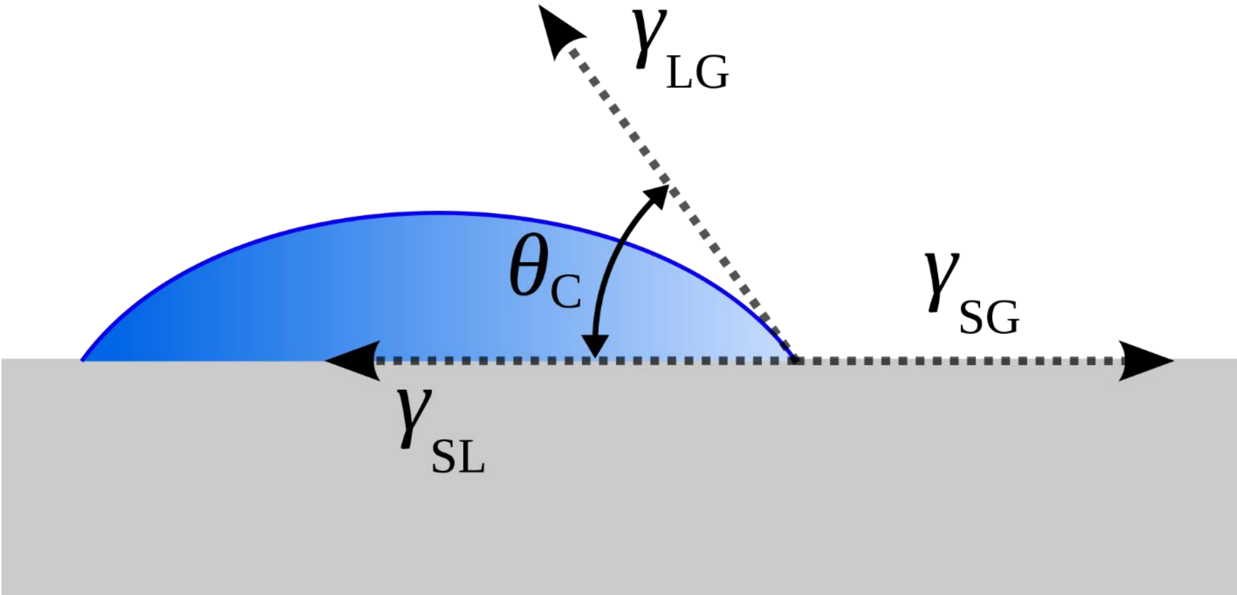

Fig. 3: Contact angle for a liquid droplet on a solid surface [12]. Accessed from [6].

A low contact angle below 90° generally indicates favourable wetting, a contact angle between 90° and 150° indicates a hydrophobic surface which repels water, and a contact angle at or above 150° indicates that the surface is superhydrophobic and that wetting is impossible. In reality, the angle which we describe is only the static contact angle and there is also a "dynamic" contact angle which comes into play in certain applications (note that the dynamic contact angle is always larger than the static contact angle) [1]. This equation is the most basic possible for understanding the contact angle and wettability, although there are many more sophisticated ones in the literature [6]. The exact chemical treatment of the sand which makes it superhydrophobic is something which we will not go into here and involves some chemistry. An example of a chemical protocol which is used to make aluminium beads superhydrophobic ($\theta \approx 150 - 170°$) can be found at [13].

The sand grains in the demonstration are superhydrophobic so they repel water on entrance into the liquid. Since the sand fails to be wetted by the liquid, it entrains air which can be seen as a thin layer around the sand. It could now be a discussion point with students what causes the sand to form clumps which can be moulded and moved about. This can be explained if a mass of sand grains of heterogeneous shape is held together by the liquid-gas interfacial tension γ_{LG} (more familiarly known as surface tension). The sand cannot wet so there are obviously no adhesive forces between the molecules of the sand grains and the water molecules. At the interface between the thin air film and the water, the cohesive forces between the water molecules are stronger than the adhesive forces between the water and air molecules, so the water layer around a blob of sand acts like an elastic membrane which keeps a number of sand grains held together in one piece (an effect known as surface tension).

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