Advances in Colloid and Interface Science 161 (2010) 124–138

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

An introduction to superhydrophobicity

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ARTICLE INFO

Keywords:
Superhydrophobic
Rough
Lotus effect
Ultrahydrophobic
Textured

ABSTRACT

This paper is derived from a training session prepared for COST P21. It is intended as an introduction to superhydrophobicity to scientists who may not work in this area of physics or to students. Superhydrophobicity is an effect where roughness and hydrophobicity combine to generate unusually hydrophobic surfaces, causing water to bounce and roll off as if it were mercury and is used by plants and animals to repel water, stay clean and sometimes even to breathe underwater. The effect is also known as The Lotus Effect® and Ultrahydrophobicity. In this paper we introduce many of the theories used, some of the methods used to generate surfaces and then describe some of the implications of the effect.

Contents

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doi:10.1016/j.cis.2009.11.001

1. Basics of superhydrophobicity

1.1. Interfacial tensions between solids, liquids and gases

To understand superhydrophobicity we begin by considering the surface of a liquid. At the surface, molecules of a liquid have fewer neighbours than those in the bulk. The resulting difference in interaction energy manifests itself as surface tension, γ_{LV}; a force that acts to reduce the surface area of a free liquid. Traditionally, surface tension can be regarded as a force per unit length and is given in units of N m^{-1} or as energy per unit area J m^{-2} [1]. When a volume of liquid can freely adjust its shape, it does so to minimize its surface free energy and since the shape with the smallest surface area is a sphere, a droplet of a liquid tends towards this shape. However, most water droplets we see in nature do not exist as spherical shapes. Larger droplets and droplets that touch surfaces are distorted by gravity and by the interaction between the water and the solid.

By considering dimensional arguments for the force due to surface tension and that from gravity, we can see that surface tension can become dominant at small sizes. Surface tension forces scale as a function of length, R, whereas gravitational forces scale with the mass of the drop, which depends upon a length cubed, R^3, and the density of the liquid, ρ. The ratio of gravitational to surface tension forces for a droplet scales as $\rho g R^3/\gamma_{LV} R \sim R^2$ (where $g = 9.81$ m s^{-2} is the acceleration due to gravity), and so is large when the length scale is large, but vanishes as the length scale becomes small. This means that the dominant force crosses over from being gravity to surface tension as the characteristic size in a system reduces. If we plot these two lines for water on Earth as in Fig. 1 they cross at a size of 2.73 mm, which is called the capillary length for water, $\kappa^{-1} = (\gamma_{LV}/\rho g)^{1/2}$. For drops much smaller than this, as a simple rule an order of magnitude smaller (i.e. <0.273 mm), surface tension dominates. The cross-over from gravity to surface tension dominated behaviour can be seen in a simple paper-clip experiment. A large metal paper-clip lowered carefully onto the surface of water breaks the “skin” and sinks, whereas a small paper-clip remains resting on the surface of the water[1]; it does not truly float, but appears to do due to the “skin effect” of water caused by surface tension. In the natural world, insects are of a size that surface tension is the dominant force. It is, therefore, hardly surprising that, in a world full of ponds and streams, many insects (and spiders) have natural morphological adaptations that enable them to either break through the surface of water or to rest and move on its surface [2,3]. Some insects walk and skate on water and others can carry a film of air underwater that acts as an artificial gill (known as a “plastron”).

1.1.1. Interactions with surfaces

Surface tension, γ_{LV}; relates to the existence of an interface between a liquid and a vapour and is only one example of an interfacial tension. When a droplet of water rests on a solid, two further interfaces, the solid–liquid and solid–vapour, become relevant and also provide interfacial tensions γ_{SL} and γ_{SV}. The balance between these three interfacial forces determines whether a droplet resting on a solid will eventually be pulled out into a film or whether it will remain as a droplet and, if so, the extent of its footprint on the solid surface. On a smooth and flat surface the interaction energy per unit area for a dry surface is γ_{SV}, but for the same surface coated in a thin layer of a liquid there are two interfaces with a combined interaction energy per unit area of $\gamma_{SL} + \gamma_{SV}$. The condition for film formation on a smooth and flat surface is therefore that the energy is lowered [4,5], i.e.

$$S = \gamma_{SL} + \gamma_{LV} - \gamma_{SV} > 0 \qquad (1)$$

where S has been defined as the spreading power. When the surface is complex in shape, such as at a join between fibres, droplets will be drawn into non-spherical shapes as they try to minimize their total surface free energy by varying the relative areas of the three interfaces, whilst maintaining their volume [6]. The size of droplet will determine to what extent gravitational energy is also a controlling factor. For example, a small droplet of water resting on a horizontal surface will adopt a shape close to a spherical cap, whereas a larger droplet will be flattened into a puddle by gravity.

When a film is not formed and a droplet remains on a surface in a partial wetting state, there is an equilibrium contact angle, θ_e, at the edge of the droplet. This is the tangent angle of the liquid–vapour interface at the three-phase (solid–liquid–vapour) contact line (Fig. 3). The contact angle is independent of droplet size and is described by the Young equation [1],

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

This concept of a single equilibrium contact angle is an idealized view and does not take into account contact angle hysteresis and how the droplet arrived at its resting state through advancing or receding on the surface. For smooth and flat surfaces and water the lowest possible contact angle is 0° (although this can correspond with many values of S) and the highest possible angle is probably less than 120° and is found on fluoropolymers, such as PTFE (Teflon®).

1.1.2. Superhydrophobicity of leaves

The leaves of the sacred Lotus are unusual in that water rolls off them in balls with contact angles much greater than that on flat PTFE. As droplets roll away they gather and transport dust and leave the surface of the leaves clean; this has become known as the Lotus effect® [7,8]. Highly mobile droplets of water on leaves with a contact angle in excess of 150° appear to be quite common in the plant world, example crop plants including the cabbage family (*brassica*), garden peas (*Pisum sativum*) and Taro (*Colocasia esculenta*) and ornamentals including Hosta (*Hosta*), Lady's Mantle (*Alchemellia*) and Lupin (*Lupinus*) (Fig. 2).

The leaves achieve this effect by creating a surface that is both rough and hydrophobic. The roughness enhances the effect of the surface chemistry to produce the superhydrophobicity. Because the waxes plants use to create superhydrophobicity are quite oleophilic, the contact angle to oils is quite low. In this case the roughened waxes increase the interaction of the oil with the surface and cause the leaves to be self poisoning, i.e. oils spread on them better (wider in extent and faster) than they do on equivalent flat surfaces.

1.2. Hydrophobicity, hydrophilicity and superhydrophobicity

A completely hydrophilic (or wetting) surface is one on which a film forms so that Eq. (1) is valid and for $S = 0$, Eq. (2) shows the threshold for this corresponds to $\theta_e = 0°$. A completely hydrophobic surface would be one for which it was energetically unfavourable for a

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[1] For a video of the paper-clip experiment see: http://www.naturesraincoats.com/Introduction.html.