



Non-stick water

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Adding a simple powder to a drop of water gives it remarkable properties: the powder-coated drop no longer sticks to surfaces, and moves by rolling, much as a solid sphere would.

Much to the consternation of adults, a broken mercury thermometer is a source of delight to a curious child absorbed by the spectacle of the silvery beads that elude capture. The epithet 'quicksilver' aptly describes the droplets, which seem to roll rapidly on the surface much like a solid marble. This unusual behaviour elicits a host of questions that are relevant to scientists in diverse fields: from chemists and engineers interested in the dynamics of drops, to astronomers interested in the stability of rotating stars and planets. How and when can liquid droplets actually roll on a surface? How fast can they move? Can they be controlled? And to what end?

On page 924 of this issue¹, Aussillous and Quéré describe the results of experiments that begin to address these issues. One motivation for these studies was provided by the need to understand the wetting properties of surfaces with different affinities for liquids. These include hydrophobic (water-repellent) surfaces, which are important in industrial processes, such as metal refining, and biological processes, such as cell motility. Traditional methods of creating these surfaces rely on chemical treatments; a familiar example is wax paper on which water will form beads.

But none of these techniques is particularly robust or long lasting, except in very clean environments. Moreover, the contact angle between the water-repellent surface and the water droplet, which characterizes the degree of hydrophobicity, cannot be increased much beyond 120° using purely chemical means. To make a super-water-repellent surface (one with a contact angle greater than 120°) requires new tricks.

In the past five years, chemical methods have been supplemented by a structural approach. On rough surfaces, contact angles of up to 175° have been achieved with water

droplets². On these super-hydrophobic surfaces, the water cannot enter the microscopic chasms in the roughness because the pressure required is too high. Therefore, the droplet is in contact with only a small fraction of the solid, much like an Indian fakir on a bed of nails, and the effective contact angle becomes large.

Aussillous and Quéré¹ have ingeniously inverted these ideas. They add a drop of water to a powder of silane-coated spores of the club moss *Lycopodium*, and stir the mixture until it yields nearly spherical, composite droplets. The powder-coated droplets are non-wetting—the resulting liquid marble will even float on a pool of water. The droplet is also a soft solid: it has an elasticity that arises from surface tension, and can bounce and roll without leaking.

The properties of these liquid marbles are brought to the fore by the lack of interaction with the underlying surface. In contrast, most liquids, such as water on smooth glass, are partially wetting, and solid-liquid interactions dominate, leading to a finite contact angle (Fig. 1a). Compared with partially wet-

ting liquids, the geometry of contact is qualitatively different for non-wetting liquids because the angle of contact is 180°, and the droplet shape resembles that of a flattened sphere (Fig. 1b). Previous theoretical investigations of non-wetting droplets³ predicted behaviour that seemed unusual and controversial. But the difficulty of achieving perfectly non-wetting surfaces prevented the theory from being tested quantitatively. Now, using their non-wetting liquid marbles, Aussillous and Quéré show that these pristine soft solids do behave unusually.

Theory tells us that, for static liquid marbles, the size of the contact area is determined by the balance between gravity (which favours contact) and capillary forces (which oppose it). The geometry of contact also dictates what happens when the marbles begin to move. A non-wetting droplet has the ability to roll without slipping on a surface that is only slightly inclined, much as a solid sphere would. By contrast, partially wetting droplets can remain stuck even on a vertical window pane. When these partially wetting droplets move they slide rather than

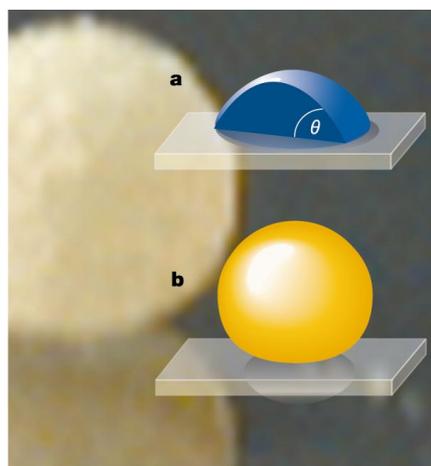


Figure 1 **Wetting and non-wetting drops.** a. A small partially wetting droplet on a solid surface has a finite contact angle, θ , determined by the behaviour of the vapour-liquid-solid system. The wedge-like shape of the contact zone controls both the statics and the dynamics of these partially wetting droplets⁴. b. Non-wetting droplets, such as the 'liquid marbles' created by Aussillous and Quéré¹, have an effective contact angle of 180° and resemble slightly flattened spheres. These liquid marbles, one of which is shown in the background and overleaf, have a different contact geometry from partially wetting droplets, and so have very different static and dynamic behaviours.

roll because their motion is controlled by the wedge-like geometry of the solid-liquid interface⁴ in Fig. 1a.

What happens to non-wetting droplets when they move on a slightly inclined plane? The velocity of the rolling marbles is ultimately determined by the competition between gravity (acting on the mass) which speeds them up, and internal fluid dissipation (in a region determined by the contact area), which slows them down. Theory predicts³, and experiments with liquid marbles now show¹, that larger droplets roll more slowly than smaller ones. This seemingly paradoxical result has a simple origin: larger drops have a larger contact area, which increases more rapidly than the volume (mass) as the size of the drop increases. So smaller drops should roll faster than larger ones, as long as the drops remain nearly spherical.

The behaviour of the liquid marbles is even more dramatic when they move rapidly. If the surface on which a marble rests is tilted to large angles, the droplet starts to spin rapidly and is transformed into a wheel-like disc with a thin web-like hub, reminiscent of planetary rings. At these high velocities the inertial forces due to rotation can greatly deform the drops. The possibility of such large deformations led Henri Poincaré and Lord Rayleigh to consider freely spinning toroidal shapes⁵ more than a century ago.

Later considerations suggested that such shapes are unstable⁶. In the new study¹, the presence of the inclined plane seems to be sufficient to stabilize the spinning wheel, and as soon as the drop either lifts off the plane or leaves the edge, the wheel-like shape is no longer stable and it rapidly morphs into a stable peanut-like shape. By looking closely at successive snapshots we can follow the evolution of the instability (see the image at the top of the previous page). But this still leaves open the details of the stabilization mechanism. Aussillous and Quéré's simple method for producing freely spinning drops will hopefully invigorate Earth-bound experiments on a centuries-old problem, complementing gravity-free experiments in space^{7,8}.

The ease with which these liquid marbles can be manufactured and moved, coupled with the relatively large velocities that can be achieved, makes them suitable for use in rapid, wear-free micromachines, such as electromechanical actuators and valves. Another possible application could be in lubrication, either as individual liquid ball-bearings or as a confined emulsion. But before such applications can be tackled, questions of how robust the drops are, and

the way their behaviour changes with age, need to be addressed.

Finally, we may not have to look far for situations that favour the production of these liquid marbles. The leaves of plants such as the lotus⁹ have many closely spaced, stiff, waxy protruberances, and many biological surfaces are hairy; a combination of chemistry and structure keeps the surfaces dry (and clean) by minimizing the effective area exposed to contaminants. Wet, dusty environments should also favour the formation of non-wetting droplets, which may play a role in transporting powders. Analogues of liquid marbles might also be relevant in cell biology, where adherent cells sometimes move by rolling¹⁰. As for mercury itself, alas it deceives the eye



and is not perfectly non-wetting, although mixing it with a powder should probably do the trick. Nonetheless, it is evident that there is still much to marvel at in a tiny droplet, if we choose to observe it with the delight of a child's eye.

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Structural biology

Chlorophylls galore

Werner Kühlbrandt

A high-resolution crystal structure of photosystem I, part of the machinery that performs photosynthesis, reveals how an extensive array of chlorophylls uses solar energy to transport electrons.

As more and more genomes are decoded, the need to understand in detail the molecular mechanisms of the encoded proteins becomes pressing. This is particularly true for proteins found in cellular membranes, as the genes encoding membrane proteins account for roughly a quarter of most genomes. A prerequisite for understanding how a protein works is knowledge of its precise three-dimensional crystal structure, but so far such structures are available for only a few membrane proteins. However, the energy-converting proteins found in bacterial and plant photosynthetic membranes, which carry out one of the most fundamental processes in biology, have yielded to crystallography more readily than others.

Now, on page 909 of this issue¹, Jordan and colleagues report the crystal structure of photosystem I, a large photosynthetic assembly of membrane proteins and other factors, at 2.5 Å resolution. The structure is the culmination of decades of painstaking work in the authors' labs to perfect both the biochemical preparation of the complex and the quality of its crystals.

There are two different but related forms of photosystem, known as type I and type II. The most ancient and primitive photosynthetic bacteria have either one or the other, but plants and cyanobacteria have both, and use them in sequence to convert solar energy into chemical energy (Fig. 1). Essentially, photosystems use the excitation energy of

sunlight, absorbed by chlorophyll, to extract electrons from a substrate and push them through the membrane in which the photosystems sit, creating an electrochemical gradient across the membrane. For photosystem I the usual substrate is a small, soluble redox protein called plastocyanin; for photosystem II, it is water. The electrochemical gradient powers the production of the energy-storing molecule ATP and, directly or indirectly, leads to the biosynthesis of nearly all organic matter on our planet.

One of the waste products of photosynthesis is oxygen, and photosynthesis by cyanobacteria is thought to have been the main reason that oxygen levels in the Earth's atmosphere rose to the point at which animal life could develop about 2 billion years ago. Since then, the photosystems embedded in the cell membranes of cyanobacteria have barely changed. These microorganisms were the direct precursors of chloroplasts, the photosynthetic organelles in land plants and algae, so the photosystems in cyanobacteria and chloroplasts are quite similar. Some species of cyanobacteria that live in hot springs have more rugged photosynthetic complexes than do chloroplasts. Jordan *et al.*¹ found these hardy photosystems to be particularly suitable for crystallization, and this was part of the key to their success.

The structure described by Jordan *et al.*¹ reveals photosystem I to be a bewilderingly complex assembly of no fewer than 11 differ-