How do drops spread over rough surfaces?

Contact angle hysteresis generated by strong, dilute defects.

Mathilde Reyssat and David Quéré

Journal of Physical Chemistry B 113 (2009) 3906

Recommended with a Commentary by Julia Yeomans, Oxford University

Contact angle hysteresis, the difference between the advancing and receding angles of a drop, controls how difficult it is to push the drop across a surface. It is a consequence of the contact line pinning on microscopic inhomogeneities on the substrate. Contact angle hysteresis is notoriously difficult to measure because it depends on the details of the surface disorder, and on the measurement protocol. However it is important because of its implications for, for example, the spreading of inks and paints and microfluidic flows.

Hydrophobic surfaces which are bumpy on a micron length-scale can become superhydrophobic. Droplets can sit on top of the bumps, in the Cassie-Baxter, or fakir, state so that the interface beneath them is a composite of a liquid-air and a liquid-solid boundary. Fakir drops have a high contact angle, which can approach $180°$, and they roll very easily. It is not hard to make superhydrophobic surfaces, wax-covered sand will do, but much more difficult to manufacture regular roughness, such as lattices of posts, which can be used for quantitative experiments.

Reyssat and Quéré use a mini Fakir's carpet for their experiments. This is a superhydrophobic surface which is made up of cylindrical posts arranged as a regular lattice. The posts are of silicon coated with a fluropolymer. They are circular with radius 1.2 μm, have height 6 μm and spacing $\sim 10\mu m$. Reyssat and Quéré placed tiny drops on the surface and tilted it. They measured the contact angle hysteresis at the point where the drop started to roll for different post concentrations.

This set-up has several advantages. Firstly the intrinsic roughness of the surface is negligible because most of the base of the drop is in contact with air, not a solid. Thus the surface is 'rough', but with controlled, non-random, topography and the dominant contribution to the hysteresis is from pinning on the posts. Secondly the authors make the substrate so that the post concentration is a slowly varying function of position. Therefore they are able to make comparisons between drops moving on a single substrate which reduces errors due to varying microfabrication conditions.

Reyssat and Quéré interpret their results in terms of a classic theory of contact angle hysteresis [1]. They argue that the hysteresis is controlled by the trailing edge of the drop which pins strongly on the posts as it is pushed over the surface. Because of the pinning the drop is deformed and the additional liquid-vapour interface acts as a spring with spring constant proportional to the surface tension and logarithmically dependent on the post spacing. The energy stored in the springs, and then dissipated as the interface moves forward, is the primary contribution to the contact angle hysteresis. The dependence of the effective spring constant on the post spacing leads to a nonlinear variation of the hysteresis with post concentration which is reproduced by the experiments.

[1] J.F. Joanny and P.G. de Gennes, J. Chem. Phys. 81 (1984) 552.