Postprint Version

G. McHale, *Liquids shape up nicely*, Nature Materials (Invited "New & Views" item). <u>6</u> 627-628 (2007); DOI:10.1038/nmat1988.

The following article appeared in <u>Nature Materials</u> and may be found at http://www.nature.com/nmat/journal/v6/n9/index.html. Copyright © 2009 Nature Publishing Group, a division of Macmillan Publishers Limited.

Liquids shape up nicely

Decorating a surface with a forest of microposts can either make it water repellent or cause the liquid to be sucked into the spaces between posts. In the latter case, the shape of a liquid on the surface can be controlled using simple design principles.

Glen McHale

School of Biomedical & Natural Sciences, Nottingham Trent University, Clifton Lane, Nottingham NG11 8NS, UK.

e-mail: glen.mchale@ntu.ac.uk

The interaction of liquids with solids is fundamental to many areas of science and technology. On a wet day we need coats to keep dry, wipers for our car windscreens and reservoirs to collect water. Nature has learnt to control water in a myriad of ways. The Lotus leaf cleanses itself of dust when it rains¹, a beetle in the desert collects drinking water from an early morning fog² and some spiders walk on water³. That control is oft en achieved not simply by adjusting surface chemistry, but by using a surface decorated with microprotrusions. If these have a surface that repels a liquid, droplets ball-up and roll off. On the other hand, if their surface is attractive to liquids, droplets are 'sucked' or 'imbibed' into the surface texture. In one step, a chemical change of the coating can switch the surface from super-water repellent to superwetting⁴. But what happens when the surface coating is only partially wetting and the surface protrusions are arranged in a regular pattern of rows and columns? As reported on page XXX of this issue, Stone and co-workers have now addressed that question⁵. By depositing

droplets of liquids onto surfaces decorated with microposts, they reveal how topography and wetting can be manipulated to design the final pattern of a liquid on such a surface, by using an exquisite selection of shapes from octagons, squares and other polygons. A droplet of a liquid deposited onto a smooth fl at surface will tend to either spread into a film or to ball up into a droplet. This intrinsic wetting tendency results from the balance of the interfacial free energies between the solid, the liquid and the vapour. Superhydrophobic surfaces increase the balling-up tendency by using surface protrusions between which it is energetically unfavourable for liquid to penetrate. If these protrusions appear as a 'bed of nails', we can imagine the liquid as skating across their tops. When the nails are thin, the liquid is supported and most of the droplet is above free space. A droplet of water hanging in air forms itself

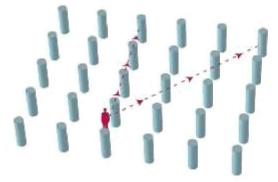


Figure 1 Standing in a forest of posts planted in a square pattern, we see lines of posts stretching ahead, behind and to our sides. We also see a line of posts along the diagonal, but the separation between successive posts is $\sqrt{2}$ greater than for those in front of us, and therefore the attraction of a liquid to the posts is different in each direction.

into a perfect sphere because of its surface tension and the same now happens for our droplet on the tips of the bed of nails. It has been shown how the tendency towards film formation can also be emphasized by the same bed of nails⁶. If the liquid–solid interaction favours a tendency to spread, the liquid penetrates into the bed, and the additional surface area from the sides of the nails cause a force that sucks the liquid into the texture. How effective this is for any given textured surface depends on both the height of the nails and the wetting properties of the liquid.

In the work of Stone and co-workers⁵, the surface protrusions are circular microposts arranged in a regular square lattice. If we imagine ourselves miniaturized and standing at the bottom of this structure we see not a 'bed of nails', but a 'forest of posts' (Fig. 1). Ahead, behind and to the side of us, posts stretch into the distance. We also see diagonal lines of posts, but these lines are not the same because each post is now a $\sqrt{2}$ distance further apart. A liquid will have different thresholds of wetting tendencies that need to be exceeded before movement in the orthogonal and the diagonal directions can occur (Fig. 2a). Moreover, when liquid motion does occur in these different directions, it generates facets at the boundaries of the liquid and these do not progress at the same speed.

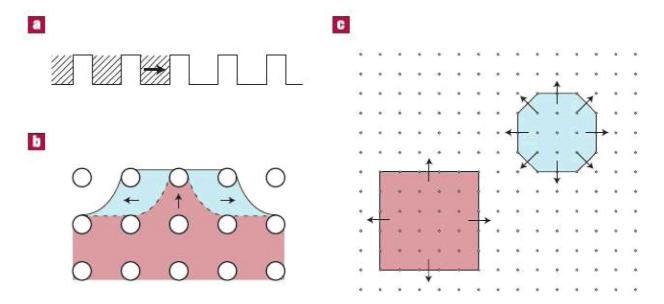


Figure 2 On a micropost-decorated surface, the threshold for imbibition depends on the height and separation of posts, and the strength of the wetting tendency of the liquid. a, Imbibition into a texture. b, Zipping motion of a facet. c, Polygonal shapes with facets.

The motion of a facet is an elegant dance involving a slow step, a fast step and a helping hand, as shown in the video accompanying the manuscript online⁵. Beginning with the liquid attached to one row of posts, its front first advances slowly towards the next row. Somewhere along the front, contact is made with a post in the row ahead and the liquid quickly attaches itself to its sides. But now the front is distorted and liquid either side of the distortion is pulled forward and quickly attaches around the post in front (Fig. 2b). The effect zips down the front in both directions moving the entire advancing liquid front forward by one row and the whole process then starts once again. In this unequal race of facets, some win and some lose, and octagonal shapes can become squares (Fig. 2c). Within our forest, the height of the posts, their spacing and the wetting properties of the liquid therefore control which facets form and the evolution and final shape of the liquid imbibed into the texture. The size of the shape formed depends on the volume of the droplet, which acts as a reservoir and which may remain as a remnant droplet or become completely drained. The result of imbibition is not a circular spot, but reflects the symmetries imposed by the lattice of posts.

When the wetting tendency is strong enough, facets advance along both the orthogonal and diagonal directions producing a transient octagonal shape. Whether it remains octagonal or

evolves into a square is determined by the relative speed along the two directions. This depends on the wetting tendency of the liquid, but can also be tuned by the height of the posts. Moreover, if the lattice of posts is changed from a square to a hexagonal pattern, hexagonal shapes can be evolved. Playing with the symmetry of the lattice completes our toolkit for shape selection.

The faceting, zipping motion and shape formation observed in these experiments droplets deposited onto a surface with a regular array of circular dots that are more hydrophobic than their surroundings⁷. However, the key difference is that these inside a texture and so further blur the distinction between wetting and quasi two dimensional porosity⁶. Controlling imbibition through the wetting properties of a liquid, and the feature height and lattice pattern enables shape selection, but also has the potential to transform a small difference in a liquid's wettability into a highly visible difference in polygonal shape. Although we do not know the precise application that will arise from this designer's toolbox of ideas, we can speculate that it might find applications in DNA electrophoresis or in a DNA microarray using shaped spots and providing more uniform fluorescence.

References

- 1. Barthlott, W. & Neinhuis, C. *Planta* **202**, 1–8 (1997).
- 2. Parker, A. R. & Lawrence, C. R. Nature 414, 33-34 (2001).
- 3. Suter, R. B., Stratton, G. E. & Miller, P. R. J. Arachnol. 32, 11–21 (2004).
- 4. Shirtcliffe, N. J., McHale, G., Newton, M. I., Perry, C. C. & Roach, P. *Chem. Comm.* (25), 3135–3137 (2005).
- 5. Courbin, L., Denieul, E., Dressaire, E., Roper, M., Ajdari, A., & Stone, H.A. *Nature Mater.* **6**, 661-664 (2007).
- 6. Bico, J., Tordeux, C. & Quéré, D. Europhys. Lett. 55, 214–220 (2001).
- 7. Cubaud, T., Fermigier, M. & Jenffer, P. Oil & Gas Sci. Technol. Rev. IFP 56, 23–31 (2001).