Algorithm exposes the energy pathways that cause super-repellent surfaces to stop working

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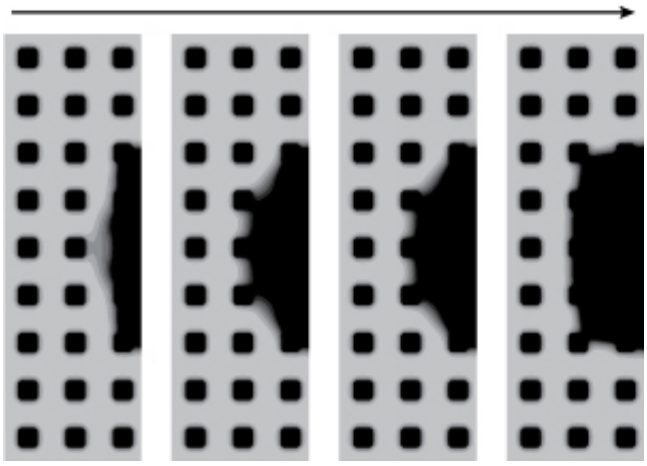

Computer simulations show that when liquid infiltrates a single gap between microscopic pillars (left), it causes extensive wetting on superhydrophobic surfaces. Credit: American Chemical Society

'Superhydrophobic' surfaces, such as anti-icing or self-cleaning windows, are remarkably effective at repelling water molecules. However, they may suddenly—and dramatically—lose their superhydrophobic features. A*STAR researchers have now identified a cause for the widespread 'wetting transition' by pinpointing how infiltration of a single microscopic groove can cause such an event.

Weiqing Ren from the A*STAR Institute of High Performance Computing and the National University of Singapore used a 'climbing string' computational technique to model a micropatterned surface that uses microfabricated pillars to trap air pockets and so repel water molecules.

When a water droplet contacts a superhydrophobic interface, it immediately beads up and forms a near-perfect sphere. Under conditions of thermal or vibrational stress, however, the water droplet collapses and fully wets the substrate. This transition occurs when enough work is supplied to cross a bottleneck, known as an energy barrier, connecting the wet and dry states.

Identifying where energy barriers occur on micropatterned surfaces could dramatically improve their manufacture. A promising way to study this problem is by using computer models of 'minimum energy paths' (MEPs), which are intermediate structures during the transition between two states. Currently, most algorithms are designed to only identify the points in a system where energy minimums occur; the unstable nature of energy barriers makes them trickier to spot.

Ren's method strings together the wet and dry minimum energy states through a smooth curve. An algorithm then seeks out MEPs available for the transition by shifting the string's endpoint to higher and higher energies (see video). This changes the string shape and eventually a 'saddle point' emerges when the physical forces acting on the curve reach a steady state. The shape of the saddle point corresponds to the energy barrier.

"Unlike other techniques, the climbing string method gives direct control over the energy of the evolving endpoint—guaranteeing that the computed saddle point is directly connected to the particular energy minimum," says Ren.

Simulating a superhydrophobic grid of microscopic pillars with the climbing string algorithm revealed the mechanisms of wetting in striking detail (see image). The critical saddle point proved to be the entry of a small quantity of liquid into a single groove between micropillars. Crossing this barrier enabled the liquid to propagate laterally across the surface in a stepwise fashion, often nucleating from a central point before zipping along the grooves and filling them.

"By numerically studying energy landscapes, we now have a quantitative basis for designing optimized patterned surfaces in engineered systems," says Ren.

More information: Ren, W. Wetting transition on patterned surfaces: Transition states and energy barriers. *Langmuir* 30, 2879–2885 (2014). dx.doi.org/10.1021/la404518q

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