WHEN WATER DOESN'T WET

Wet metal is everywhere: domestically, industrially, technologically. It has surely been one of the most pervasive materials systems ever since swords were tempered and armour rusted. Today the interface of metals and aqueous solutions is central to electrocatalysis and biomedical prosthesis, to name just two instances. Yet there remains plenty that is not understood.

Metals are generally considered hydrophilic, because of the possibility of bonding between oxygen lone pairs and the surface metal atoms. Water seems to wet platinum, gold and other metals, although experiments are often complicated by surface impurities. But the story of how a water film evolves on such noble metals is not a simple one, as a new study illustrates¹.

It was once supposed that, to maintain hydrogen bonding between adjacent water molecules, water on metals will adopt a corrugated structure in which only half of the molecules bind to the surface: essentially a two-dimensional slice of ice. But a water monolayer on Pt(111) has instead a flat structure in which there is alternating surface bonding via oxygen and hydrogen². This arrangement leaves no free, uncoordinated OH bonds at the surface available for hydrogen bonding.

That would seem to imply that, odd as it may sound, the water monolayer is itself hydrophobic. And so apparently it is: ice grows on a

monolayer of water on Pt(111) above 135 K as crystallites that do not wet the surface³. This illustrates how important the directional hydrogen bonding of water is for its interfacial behaviour: enforced reorganization of the network of hydrogen bonds can here make water (or ice) unlike itself — a situation inconceivable for simple liquids.

But although it isn't hard to rationalize this 'hydrophobic' water layer at cryogenic temperatures in terms of a lack of dangling bonds, simulations by Wang *et al.* showed that similar non-wetting behaviour pertains even at room temperature, where some dangling bonds remain⁴. Here there is competition for hydrogen bonding to water molecules in the (hexagonally ordered) monolayer: neighbours within the monolayer compete more successfully than other water molecules sitting on top of the layer, with the result that — above a threshold of charge density within the substrate — additional water molecules cluster into non-wetting droplets sitting on the monolayer.

This picture is refined by Limmer *et al.*¹ whose simulations confirm that the preferential orientation of dangling OH bonds towards rather than away from the surfaces of Pt(100) and (111) depletes the opportunities for a water monolayer to bond with bulk water on top, in effect passivating the surface. Even though oxygen atoms

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offer hydrogen-bonding acceptors, the asymmetry of this situation makes the monolayer hydrophobic. There are then large density fluctuations in bulk water close to the interface, and the monolayer provides a favourable environment for solvating hydrophobic particles.

Limmer *et al.* suggest that this situation may not be unique for metals, but could occur also for clays and other oxide minerals, perhaps even for biological surfaces. The preponderance of hydrogen-bond acceptor sites at the monolayer surface also implies that hydronium ions might congregate there, perhaps enhancing platinum's facility for catalysing hydrogen evolution in electrolysis. □

References

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NANOSTRUCTURED ALLOYS

Large tensile elongation

A nanostructuring processing route that leads to submicrometre grains and nanometric oxide particles uniformly distributed within the grains' interior is used to fabricate molybdenum alloys that have both exceptional high strength and ductility at room temperature.

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Both bottom-up and top-down approaches for nanostructuring bulk crystalline metals and alloys have led to solid improvements in the physicochemical properties of these

materials^{1,2}. In the bottom-up approach, bulk nanomaterials are fabricated by assembling individual atoms or by consolidating nanoparticulate solids. The top-down approach, instead, is based

on grain refinement at the nanoscale through severe plastic deformation³. For both approaches, the formation of various structural elements — such as grains, lattice defects, or spatially segregated