Physicists shed new light on how liquids behave with other materials

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Using a range of theoretical and simulation approaches, physicists from the University of Bristol have shown that liquids in contact with substrates can exhibit a finite number of classes of behaviour and identify the important new ones.

Their findings, published in the *Proceedings of the National Academy of Sciences* (*PNAS*), challenge the accepted wisdom on wetting and drying phase behaviour.

The authors provide a firm conceptual framework for tailoring the properties of new materials, including finding super-repellant substrates, such as expelling water from windscreens, as well as understanding hydrophobic interactions at the length scale of biomolecules.

When a liquid such as water is repelled from a solid substrate, the drop created exhibits a large contact angle. This is known as a hydrophobic state, or superhydrophobic if the contact angle is very large, so that the drop forms a near spherical shape.

By contrast, if the substrate attracts the liquid sufficiently strongly—in other words, a hydrophilic substrate—this creates a small contact angle and the drop spreads over the surface.

Whether a surface is hydrophobic or hydrophilic is determined by the degree of molecular attraction between the substrate and the liquid.

Controlling the attraction is key to the wettability of substrates, which determines how many physical and biological systems function. For instance, plant leaves are often hydrophobic, allowing them to remain dry during rain so that gas exchange can occur through their pores. However, liquids such as paints, inks and lubricants are required to spread out to coat or 'wet' surfaces.

Building on early insights gained by former Bristol Ph.D. student Dr. Maria Stewart, Professor Bob Evans and Professor Nigel Wilding applied a number of theoretical and simulation techniques to realistic fluid models in order to study the properties of hydrophobic and hydrophilic substrates.

They discovered rich and unexpected behaviour such as divergent density fluctuations associated with the phenomenon of 'critical drying' at a superhydrophobic substrate.

Professor Evans said: "Clarifying the factors that control the contact angle of a liquid on a solid substrate is a long-standing scientific problem pertinent across physics, chemistry and materials science. Progress has been hampered by the lack of a comprehensive and unified understanding of the physics of wetting and drying phase transitions. Our results show the character of these transitions depends sensitively on both the range of fluid-fluid and substrate-fluid interactions and the temperature."

Professor Wilding added: "Our work has uncovered previously unrecognised classes of surface phase diagrams to which most experimental and simulation studies of liquids in contact with a substrate belong. A particularly interesting feature relates to water near superhydrophobic substrates where one observes the phenomenon of `critical drying' as $\theta \rightarrow 180°$. This is signalled by divergent density fluctuations which lead to rich structural properties including fractal arrangements of vapor bubbles near the substrate."

More information: Robert Evans et al. A unified description of hydrophilic and superhydrophobic surfaces in terms of the wetting and drying transitions of liquids, *Proceedings of the National Academy of Sciences* (2019). DOI: 10.1073/pnas.1913587116

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