New understanding of the 'dewetting' process

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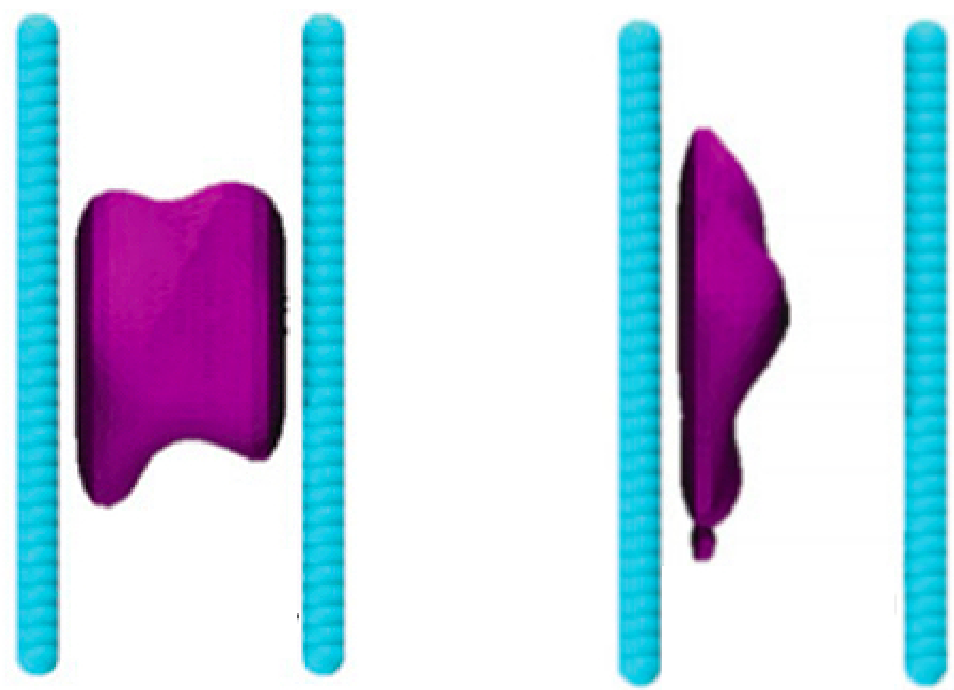

A simulated vapor tube (left) and isolated vapor cavity (right).

When a material, typically a liquid, is confined by surfaces that it doesn't like, the material can be expelled from the confining region in a process called "dewetting."

University of Pennsylvania researchers have now discovered a new facet of this "dewetting" process, showing it is easier to initiate than previously believed. Using computer modeling, they showed how variations in the density of water molecules that are confined between two hydrophobic surfaces, can speed along this process.

Better understanding of dewetting would be helpful in both controlling it and promoting it. On one hand, dewetting decreases the stability of thin films, such as the ones found in smartphone displays. On the other, dewetting is crucial to the function of the water-repelling superhydrophobic surfaces. Dewetting is also implicated in the initiation of boiling. The first places where bubbles appear in a boiling pot of water have to do with dewetting at certain surface sites.

The research was led by Amish Patel, the Reliance Industries Term Assistant Professor of Chemical and Biomolecular Engineering in Penn's School of Engineering and Applied Science, along with group members Richard Remsing and Erte Xi. Srivathsan Vembanur and Shekhar Garde of Rensselaer Polytechnic Institute and Sumit Sharma and Pablo Debenedetti of Princeton University also contributed to the study.

It was published in the *Proceedings of the National Academy of Sciences*.

"As with many physical and chemical processes, an energetic barrier must be overcome before dewetting can occur," Patel said. "The time it takes for the process to occur depends on the height of this barrier. And, if the barrier is too high, dewetting may never occur for all practical purposes."

Prior to this research, scientists assumed that the formation of a "vapor tube," or a cylindrical bubble of vapor that spanned the gap between the two surfaces, was a prerequisite for the dewetting process to begin.

"The previously accepted theory suggested that whenever vapor tubes formed, they would begin to grow and push out the remaining water only if their diameter was big enough," Patel said. "If the diameter isn't big enough, the tube collapses. The energy required for formation of a vapor tube of a certain critical size—that's the barrier the dewetting process has to overcome."

To better understand how vapor tubes form and to understand their role in dewetting, the researchers used molecular simulations in conjunction with a technique known as indirect umbrella sampling. This technique allowed them to characterize water-density fluctuations in the gap between two simulated nanoscale surfaces separated by a range of distances.

Visualizing their simulations revealed a new phenomenon: In the initial stages of dewetting, stable bubbles of vapor to form near one surface, rather than span both surfaces.

"As these voids grow, it's possible for them to reach across the surface and make a tube," Patel said. "But, by that point, the vapor tube is already bigger than the critical size predicted by the previous theory and also requires less energy to form. As a result, it's easier to induce dewetting through this new pathway than by starting with a vapor tube and growing it."

Dewetting can also be important in protein folding and assembly, wherein water must be expelled between the parts of the protein or proteins about to come into contact.

"Proteins have hydrophobic, water-repelling patches that are relevant to how they fold and assemble," said Patel. "Water is everywhere as these two surfaces approach one another, but, when they get close enough, we think that dewetting may occur before they actually touch."

Consideration of this pathway could allow for a better understanding of dewetting processes in protein interactions and assembly, as well as in non-biological systems that self-assemble in aqueous environments.

More information: Richard C. Remsing et al. Pathways to dewetting in hydrophobic confinement, *Proceedings of the National Academy of Sciences* (2015). DOI: 10.1073/pnas.1503302112

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