How does a thin film rupture?

Tobias Kerle, Jacob Klein, Rachel Yerushalmi-Rozen

From
Physics World
August 1998

ISSN: 0953-8585

Institute of Physics Publishing
Bristol and Philadelphia

How does a thin film rupture?

From Tobias Kerle and Jacob Klein in the Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot, Israel, and Rachel Yerushalmi-Rozen at the Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheba, Israel

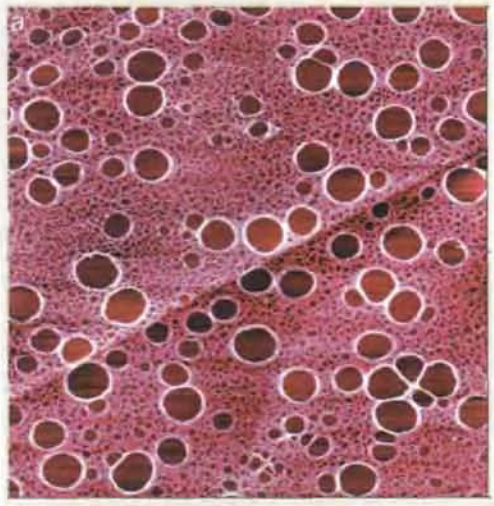
Many liquids will spread uniformly on a surface, a process known as wetting. But an equally common process is dewetting, in which a liquid is forced to spread on a surface that it does not wet and subsequently breaks up into many small droplets. The patterns formed by these droplets were first studied by Rayleigh and Marangoni about 100 years ago, and today there is still much interest in dewetting and its effect on the stability of thin layers. Such thin films are extensively used in technologies ranging from microelectronics to cosmetics, and the stability of the film is crucial to its effectiveness.

Ultimately, whether a liquid wets or dewets a surface depends on the balance of surface and intermolecular forces, and these are well understood. So it may come as a surprise that the physics of dewetting, particularly in very thin films, is still a matter of controversy. Recent experimental work has explored the mechanisms involved in dewetting, and has produced some intriguing results.

Dewetting starts when a liquid film ruptures. Holes form to expose the surface underneath, and these then grow and merge together. The initial rupture can be caused by two very different mechanisms. The first involves surface undulations of thermal origin. In thin unstable films these undulations grow spontaneously until their depth equals the film thickness, at which point a hole forms. A hydrodynamic analysis suggests that the fastest growing undulations have a wavelength that is proportional to h^2/a, where h is the thickness of the film and a is a characteristic molecular length of the liquid, typically a few angstroms. This implies that adjacent holes are correlated, and that their spacing should be similar to the wavelength. The analysis also suggests that the expectation time for holes to form varies as h^5.

A quite different pathway for film rupture is by heterogeneous nucleation. This occurs when holes nucleate on dust or air bubbles in the film, or on imperfections in the substrate, such as dislocations and grain boundaries. These nucleation sites are distributed randomly and so there is no correlation between the positions where holes form.

Which of the two mechanisms dominates? To answer this question researchers usually examine the hole pattern as it forms. Thin polymer films are often used in such studies because the interactions within the film and at the surface are mainly due to van der Waals forces, which simplifies the interpretation of the results. Moreover, polymer films are of practical importance in a variety of low- and high-tech applications (see *Physics World* August 1995 pp30–36).



(a) Pompe and colleagues observed that the holes formed by rapidly drying a film of a protein solution have two characteristic sizes. This is also evident in the distribution of hole sizes (b). They suggest that the large holes form through heterogenous nucleation, while small holes are caused by the growth of thermal undulations.

Early work on the dewetting of these polymer films by Gunter Reiter, then at the Max Planck Institute for Polymer Research at Mainz in Germany, showed that the density of holes varied as $1/h^4$, as would be expected if the holes form through the growth of thermal undulations and the hole spacing depends on h^2. However, more recent work suggests that heterogeneous nucleation, rather than undulation growth, plays the dominant role. And studies of gold films by Paul Leiderer and colleagues at Konstanz University have revealed both mechanisms taking part – large holes were attributed to heterogeneous nucleation, while a distribution of smaller holes was thought to be caused by the growth of thermal undulations.

In the latest development, Wolfgang Pompe and colleagues at the Technische Universität Dresden in Germany have reviewed the earlier evidence and suggest a different approach to studying the dewetting problem (*Phys. Rev. Lett.* 1998 **80** 2869). They spin-cast a solution of protein in weak acetic acid onto a solid surface. As the water in the sample evaporates, the film becomes thinner and eventually dries at a rate that depends on the humidity. This leaves behind a pattern of holes defined by the dried protein at their edges. Such a multicomponent system is considerably more complicated than nonvolatile liquids, and could experience complex dynamic processes as the film becomes thinner.

Intriguingly, the researchers found that fast-drying films produced both large and small holes (see figure), while films drying more slowly only produced large holes. They suggest that for slower evaporation rates the holes are nucleated – probably by crystal steps on the substrate – and grow to cover the entire surface while the film is still relatively thick. In fast evaporating films, however, the nucleated holes do not have time to cover the entire surface before the film becomes thin enough to be ruptured by surface undulations. The researchers therefore conclude that holes generated by nucleation and thermal undulations coexist in the dewetted film. This is consistent with the earlier studies on gold films, but the evidence is arrived at in a very different way.

So where do we go from here? Unlike the arrangement of holes formed through dewetting, the dynamic aspects of hole formation have barely been explored. In particular, the rather striking prediction that the expectation time of hole formation due to undulations should vary as h^5 has not yet been confirmed, and future work will certainly address this issue.

The ideal solution would be to study the evolution of the undulations directly, but in a way that does not perturb them. We recently made a step in this direction by using optical phase-interference microscopy to monitor the growth of surface undulations in a dewetting film.

A clear result is emerging from all of these studies: the amplification of thermal undulations in thin films provides a pathway for rupture and subsequent dewetting, but this can be bypassed if nucleated holes expand to cover the surface first. By understanding these dynamic phenomena, we will gain important insights into the stability of thin liquid films.