To Bead or Not to Bead?

That is the question when researchers make ultrathin coatings

By PETER WEISS

If an optical coating on a lens beads up or becomes filled with holes like a slice of Swiss cheese, the lens may become foggy or distort light. Similarly, an insulating glaze in a microelectronic chip may allow short circuits if the film breaks as it is deposited. In the eye, the fine coating of lubricating tears disintegrates too easily in some people, causing an uncomfortable dryness.

The tendency of thin films of liquids to retract, or dewet, from surfaces challenges the ingenuity of engineers and designers of a wide range of technologies and products—from optics and microelectronics to eye drops, paints, and multilayer polymer packages for food. "Thin films often are finicky little beasts," says Pierre Wiltzius of Lucent Technologies' Bell Labs in Murray Hill, N.J.

Researchers have devised treatments for surfaces and coatings that promote the spread of uniform films even when the surface or the overlying film naturally resists such wetting, as they commonly do. To eliminate long-recognized seeds of dewetting such as dust and rough spots on surfaces, thin-film makers use clean-rooms and meticulously polish or chemically treat substrates on which the films will lie.

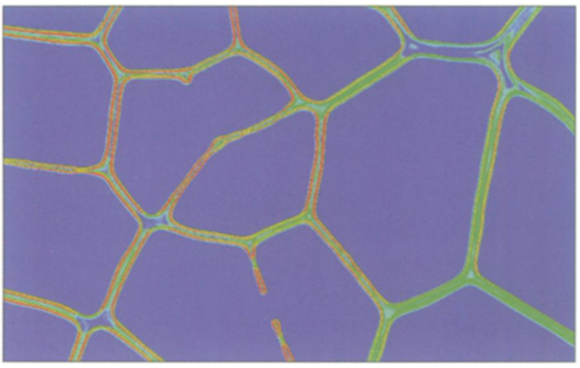
Dutch chemist Anton Vrij hypothesized more than 30 years ago that even in the absence of defects, extremely thin films of liquid spontaneously self-destruct under certain conditions. For soap films in air, he predicted that waves would arise unbidden from the thermal jiggling of molecules or atoms in the film and then amplify at a favored frequency until the waves broke through the surfaces.

Other researchers later extended his theory to liquid films on solid surfaces, where the surface waves would shatter the film into droplets or riddle it with holes. Only in the past few years have experimenters found persuasive evidence that this phenomenon actually exists, and opinion remains divided on whether it has practical consequences.

The extension of Vrij's theory dictates that a distinctive pattern of undulations on a film's surface would arise before the film disintegrated. The process is called spinodal dewetting because scientists noted sharp peaks, or spines, when they graphed properties of materials separating in a similar process.

The predicted patterns of surface undulations were not seen with certainty, however, until Jörg Bischof and his colleagues at the University of Konstanz in Germany finally made a laser snapshot of them in melted metal foils. The German team reported its findings in the Aug. 19, 1996 Physical Review Letters.

Since that discovery, researchers from around the world, including some of the Konstanz experimenters now at other labs, have presented fresh clues about spinodal dewetting. Among the new findings—some of them controversial—is evidence that this breakdown process occurs in films of not only metals but also polymers, proteins, and liquid crystals.


Reiter

In some cases of thin-film dewetting, remnants of the disintegrating film coalesce around polygonal holes (blue) before deteriorating further into droplets. The great length of the polystyrene molecules in this film, initially 60 to 70 nanometers thick, causes this temporary web with gaps about 40 microns wide.

"Now, a big part of materials science is showing this," says Alamgir Karim of the National Institute of Standards and Technology (NIST) in Gaithersburg, Md.

Liquid films become prone to spinodal dewetting, physicists say, when intermolecular forces add up to a net attraction that tugs the top of the film toward the underlying surface. Believed to be most important are van der Waals forces, which arise from displacements of electron clouds when atoms press close together. Although weak, the van der Waals forces can act over the span of many hundreds of molecules, gathering the collective muscle to break down films that are tens of nanometers thick.

Better understanding of spinodal dewetting may prove important for technologies that depend on thin films, many scientists say. Manufacturers are using thinner and thinner films that become more and more likely to dewet in this way. Preserving films that are poised to self-destruct could pose a special challenge, since old strategies of cleaning and polishing would be useless against an inherent tendency to break down. Spinodal breakdown may limit the thinness that coatings can attain, Karim says.

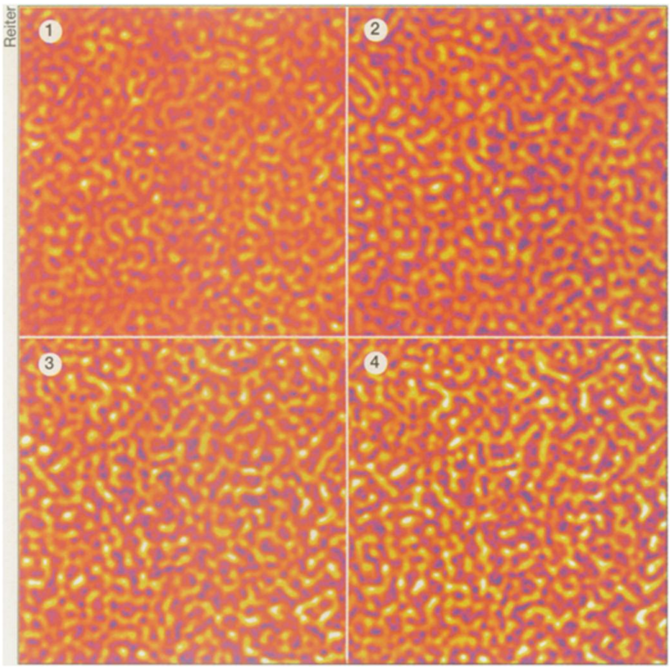
On the other hand, some scientists argue that spinodal dewetting remains on the margin of technological significance. Françoise Brochard-Wyart of the Curie Institute in Paris salutes the new findings as important basic research, but she questions their practical relevance.

"The film has to be extremely thin for spinodal dewetting—in the range of nanometers—but in most of industry, they look at thicker films, in the range of 100 nanometers or more," she explains.

Brochard-Wyart coauthored a 1990 theoretical study that extended Vrij's theory from soap films in air to liquid films on hard surfaces. Her study and the work of Vrij and earlier researchers made testable predictions. The rate at which holes develop should depend on the film's thickness in a specific way, for example, and holes should form with a characteristic arrangement and spacing.

Recent studies have focused on patterns of dewetting in various thin films and asked whether those patterns and the rates at which they develop conform to the theory. "What people are really looking for in this field is the right kind of model systems," Wiltzius says. "One still does not have a crisp model system to really get at the heart of the science behind this. But unless you do the experiments, you won't get to that stage."

Wiltzius studies a related phenomenon



Starting at upper left, a liquid silicone thin film (red) develops increasingly larger waves in its surface as it sits for a short time on a substrate (yellow) that resists being coated by it. Over the course of about 8 minutes, wave crests (dark) heighten and troughs (light) deepen. The spinodal ripples may spontaneously lead to holes in the film and then to complete dewetting.

called spinodal decomposition, for which researchers developed convincing laboratory models only a decade ago. Such decomposition occurs when two blended liquids, such as oil and water, that are separating from each other intermingle in a transient granular pattern. It shows a patchwork similar to the corrugations on the surface of a dewetting film.

In the early 1990s, Günter Reiter, who is now at the Institute for the Chemistry of Surfaces and Interfaces of the National Center for Scientific Research in Mulhouse, France, pioneered the use of thin coatings of liquid polystyrene on silicon to observe dewetting. After the films dewetted, he counted the number of holes per unit area and found good agreement with spinodal dewetting theory.

The direct evidence for the waves underlying spinodal dewetting came in 1996 from experiments with metal foils on glass. The University of Konstanz researchers briefly melted foils—25 to 50 nanometers thick—with a laser beam whose intensity varied across the foil surface. While molten, the metal began to dewet. The uneven heating made some parts of the foil stay melted longer than others and, therefore, dewet further. In the cooled, congealed metal, the researchers saw the telltale ripples of an early stage of dewetting, with a wavelength predicted by theory.

A year later, Terry G. Stange of the University of Minnesota in Minneapolis and his collaborators reported that the rate at which holes form in a film also matches the spinodal dewetting theory. These researchers had examined dewetting of polystyrene films, thinner than 25 nm, deposited on silicon. In the Aug. 10, 1998 Physical Review Letters, Karim and his collaborators from NIST and the University of Connecticut in Storrs described similar findings in the same type of films.

Yet some researchers question whether dewetting patterns are proof that spontaneous surface waves are their cause. "How valid is it to make assumptions about the early stage of an instability from things you see at a late stage?" asks Richard A.L. Jones of the University of Sheffield, England.

In the Dec. 7, 1998 Physical Review Letters, a research team led by Jones reports directly watching surface waves typical of spinodal dewetting grow at the interface between two liquid polymer layers. Using neutron beams to observe the undulations buried between a thick polystyrene layer and the roughly 100-nm-thick acrylic coating overlying it, the scientists detect the waves before any sign of actual dewetting appears. As predicted by theory, a wave of a certain preferred frequency dominates.

The data show that scientists have drawn valid inferences from late-stage dewetting patterns, Jones asserts. Although his group observed a liquid-on-liquid interface, the findings apply to liquid-on-solid studies that others have done. "The physics is pretty simple. When it's simple, it's general," he says.

The physics is complex enough, however, to have sparked disagreements.

Last year, Karin Jacobs and Stephan Herminghaus of the Max Planck Institute for Colloid and Interface Science in Berlin-Adlershof and Klaus R. Mecke of the University of Wuppertal in Germany splashed cold water on many recent findings on spinodal dewetting.

They had expected that spinodal dewetting should produce an ordered patterning of holes in liquid polystyrene-on-silicon films, which have been popular for studying the process. Instead, the group found a random arrangement. They argue that minuscule bubbles of air or other gases in the pores of the polymer, not spontaneous surface fluctuations, cause dewetting.

"In contrast to what has been frequently asserted, we show that spinodal dewetting does very probably not play any significant role in the [polymer-film] rupture process," the researchers asserted in the Jan. 23, 1998 online version of Langmuir. On the other hand, the findings for metal films, which would be bubble-free, remain valid, they argue.

The Jacobs group also reanalyzed Reiter's data on hole positions in polystyrene films and concluded that spinodal dewetting was not at work. Moreover, they found that polystyrene films remained intact in a vacuum, which would have removed gas from the film.

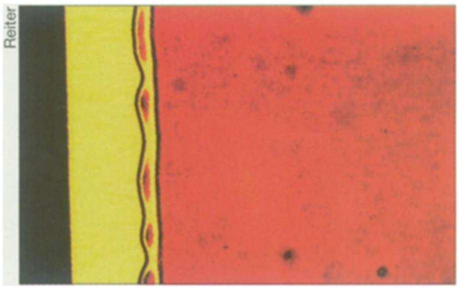
Reiter says the gas-bubble idea is "a little strange," but he offers no other explanation for Jacobs' vacuum findings. "For this particular system that I created, there may be some mystery," he admits.

The conventional wisdom about spinodal dewetting has also come under fire from an Israeli-U.S. research team. The group, led by Jacob Klein of the Weizmann Institute of Science in Rehovot, Israel, reports activity that seems to indicate spinodal dewetting in films supposed to be immune to the process. The scientists observed surface waves deepening into pits in ethylene-propylene films 100 to 200 nm thick on silicon, where they did not expect waves to amplify.

"We're puzzled," says Klein. "There may be something else at the bottom of this," he says. The group raises its questions in the Nov. 15, 1998 Europhysics Letters.

In most investigations of ultrathin film dewetting, scientists have expected to see only two distinctive patterns. Random hole patterns would signify that dust or chance imperfections were to blame. A relatively orderly arrangement would suggest a spinodal process.

Yet researchers may have overlooked much of the complexity, some groups say. Could there be a wider variety of dewetting patterns? Are more elaborate



Seen from above, a 100-nm-thick liquid silicone film (red) retracts to the right from a surface (yellow) that resists being coated by it. In this experiment, a sharp break (left edge) made in both the film and underlying silicon substrate initiates the film's ragged retreat.

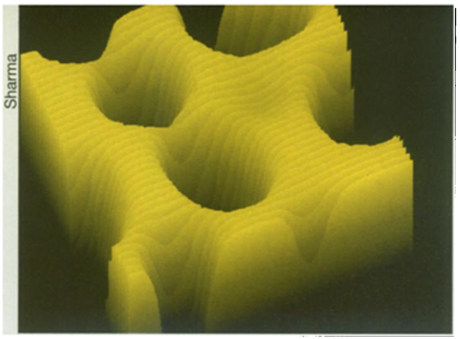
theories needed?

A new computer simulation, for example, predicts that the willy-nilly hole pattern expected from impurities could arise also from spinodal dewetting. Ashutosh Sharma and Rajesh Khanna of the Indian Institute of Technology in Kanpur discuss the simulation in the Oct. 19, 1998 Physical Review Letters. Already, Herminghaus' group has independently noted in spinodal dewetting experiments a random hole pattern like that in the simulation, although they say this pattern is temporary.

"They don't have to invoke [defects in the film] to explain the holes. This is a sort of revelation," Karim says.

In the Oct. 30, 1998 Science, Herminghaus' team also describes a disintegration much like spinodal dewetting in liquid-crystal films. This disintegration, however, is modified by the strong tendency of the film's molecules to line up with each other. The molecular interaction forced the dewetting to penetrate only the top 12 nm of the film.

In a commentary in the same issue of Science, Reiter hailed Herminghaus' experimental foray into the more complex workings of dewetting as "a major achievement." Dewetting patterns may serve as a way to measure the strength and range of the intermolecular forces in liquid films for the first time, Reiter says.



Sharma

In a recent computer simulation of "spinodal dewetting," a thin film ruptures into a pattern of enclosed holes. In spinodal dewetting, waves that arise spontaneously in the film surface ultimately penetrate to the underlying substrate. Scientists previously thought that only dust or defects in the substrate caused this Swiss-cheese pattern.

In effect, dewetting patterns can act as a "thin-film force microscope," Sharma says. In a future issue of Europhysics Letters, he, Reiter, Khanna, and other researchers will report a study in which polymer films of different initial thicknesses dewet. By measuring aspects of the dewetting patterns—for instance, the number of droplets per square millimeter—the experimenters detected the signature of van der Waals forces.

While scientists struggle to define and understand spinodal dewetting, they also are looking for ways to do something practical with it. One of the phenomenon's attractions lies in the extraordinarily small size of droplets it generates. "There is hope that one can create patterns on substrates truly at the nanometer level," Karim says.

Controlled dewetting of magnetized films, for instance, might generate an orderly array of ultrasmall magnetic droplets, perhaps as data-storage elements. Reiter says he has been working on ways to control the patterns created by spinodal dewetting and has succeeded in transforming the typical jumbled patterns into something more orderly.

Most researchers say, however, that their immediate goal is a deeper understanding of dewetting. It may, in turn, allow a closer look at the intermolecular forces at work when films become beads. □

Astronomy

More evidence for a flat cosmos

According to inflation, a theory that seeks to explain the origin of structure in the universe, the cosmos underwent an episode of enormous expansion during the first fraction of a second of its existence. Like the surface of a balloon blown up to enormous proportions, any curvature to space-time was stretched out by the expansion (SN: 12/19&26/98, p. 392). In other words, the universe should be flat.

Astronomers have now found an additional hint that the universe indeed has zero curvature. The finding comes from studies of the cosmic microwave background, the whisper of radiation left over from the Big Bang.

Two telescopes at the South Pole have recorded variations in the intensity of the microwave background on different spatial scales. One instrument examined variations on scales of $\frac{1}{4}$ to $3\frac{1}{2}$ degrees, the other on scales of 1 to 10 degrees. Inflation predicts that the variations should be greatest in patches of the sky a half a degree across—the size of the full moon—and the combination of data from the two telescopes matches the predicted pattern.

One of the instruments, Python, recently ended its 5-year tour of duty. The other, Viper, began taking measurements last February, and researchers have now finished analyzing data taken during its first few weeks of operation, says Jeffrey B. Peterson of Carnegie Mellon University in Pittsburgh. The Python and Viper measurements "tie together beautifully," he says. Peterson and Kimberly A. Coble of the University of Chicago reported the findings last month in Paris at the Texas Symposium on Relativistic Astrophysics.

"While the data are consistent with a flat universe and inflation, I do not think that the data are strong enough to rule out alternative models," notes David N. Spergel of Princeton University. Over the next year or two, new ground-based and balloon experiments that will scan a larger area of the sky and explore a greater range of wavelengths "will [more] accurately measure the microwave background fluctuations," he says.

Spergel is working on the Microwave Anisotropy Probe, a NASA satellite set for launch in 2000. It "will make the definitive measurements of the background fluctuations," he says. *—R.C.*

Sun storm squeezes Earth's ionosphere

A spacecraft has found the first direct evidence that storms generated on the sun squeeze Earth's upper atmosphere, ejecting gases into space. A satellite called Polar found that the flow of ionized gas from Earth's poles increased dramatically just as a solar storm plowed into Earth on Sept. 24 and 25.

The storm originated on the sun as a magnetized cloud of ionized gas. A shock wave generated by the storm rammed into the magnetic shell that surrounds Earth, giving enough of a kick to gas trapped in the ionosphere, a layer of the upper atmosphere, to expel several hundred tons of gas, mainly oxygen.

Researchers already knew that hydrogen, helium, and oxygen ions from the ionosphere leak into space, but they had never correlated the flow with a solar storm. Trapped in the wake of the solar wind, most of the ejected gas eventually returns to Earth. The returning gas is accelerated and heated by the same processes that create Earth's radiation belts and spectacular auroras and helps supply the raw material for these displays.

Thomas E. Moore of NASA's Goddard Space Flight Center in Greenbelt, Md., reported the findings last month at a meeting of the American Geophysical Union in San Francisco.

Before Polar, astronomers had found it difficult to detect charged particles migrating from the ionosphere. The electrical charge that naturally builds up on the surface of spacecraft, due to ionizing radiation from the sun, interfered with observations. Polar's detectors use a plume of xenon ions and electrons to dispose of any charge that builds up, enabling the craft to track the flow of ions from the upper atmosphere. *—R.C.*