tals might open up new possibilities, such as larger band gaps, that are not possible with pure dielectric materials as has been shown in experiments and theory for microwave radiation [see references cited in  $(\mathcal{S})$ ]. However, absorption of the metallic structures, as is the case for photons in the visible, could limit these possibilities. The effects of absorption, which will become important for fluorescent materials placed inside photonic crystals as well, have hardly been studied theoretically and not at all experimentally. This situation will undoubtedly change soon.

It is clear that the colloidal templating route is substantially cheaper than conventional lithographic methods to produce 3D structures with submicrometer feature sizes and that now truly 3D structures with high contrast and even metallic properties are easily obtained. Moreover, with yet another templating approach,

### SCIENCE'S COMPASS

this time extending epitaxial crystal growth procedures to the colloidal domain, my colleagues and I have been able to grow large colloidal single crystals and direct their structure and orientation (10). The time has now come to use these methods, or most likely combinations of them, to make materials that demonstrate some of the above-mentioned promise and potential. For instance, one can easily imagine using inorganic colloids, possibly fluorescently labeled, in the processes that use organic spheres as templates. And vice versa, one could use latex spheres in the process that dissolves silica. With such combinations, the airsphere crystals could be doped by placing a few dielectric particles in the air spheres to create dielectric defects, for instance, to open up a narrow transmission path in the band gap. In the same way, the conductive crystals could be made into

## PERSPECTIVES: THIN-FILM PATTERN FORMATION

# The Artistic Side Of Intermolecular Forces

#### **Günter Reiter**

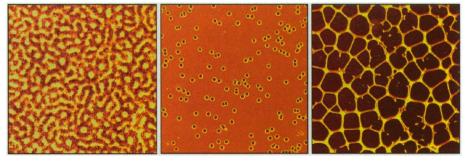
iquid films thinner than about 1  $\mu$ m are often unstable and develop various morphologies (see figure). The stability of such films may be essential, for both numerous applications and various scientific experiments, and so this behavior can be rather annoying. As reported on page 916 of this issue, Herminghaus et al. (1) have recently addressed the question of why such films are unstable. They have presented some convincing results that indicate the relevance of intermolecular forces for what they called "spinodal dewetting." It is similar to the process of spinodal decomposition, in which a binary mixture becomes unstable and moves along a cusplike curve (spinode) toward phase separation.

There is a long-standing debate about the factors responsible for the instability of thin liquid films. On the theoretical side, Scheludko and Vrij proposed some 30 years ago (2, 3) the possibility of an intrinsic instability induced by long-range van der Waals forces across the film. However, most previous experimental observations of unstable films were simply attributed to rupture of the films induced by defects such as dust particles, which, in turn, resulted in dewetting. Thus, attempts have been made to eliminate defects. Only recently have several model experiments (4-7), mostly with polymers, allowed the exclusion of initiation of dewetting by defects. Nonetheless, in many cases, it is still not clear what kind of interactions were responsible for the instability (3, 4). This is because several different morphologies, in particular wave patterns and isolated circular holes (see figure), evolved from such an instability. It was erroneously assumed that these different morphologies necessarily imply that difperhaps even more versatile metallo-dielectric crystals. Guided by theoretical calculations, it will probably not take long for these opal-based photonic crystals to be seen in a new light.

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ferent processes had generated them, mainly because early linear theories (3, 8)of spinodal dewetting were unable to predict the various possible patterns. Undulation patterns were taken as signs of spinodal dewetting, whereas the formation of isolated holes was thought to reflect an instability induced by defects or heterogeneities (5, 9). The major achievement of Herminghaus et al. (1) is that they have now shown that the same process-spinodal dewetting-can result in different patterns if the long-range van der Waals forces are coupled with various shortrange interactions. Thereby, the nonlinearities of the "wetting forces" are modified. This allows the formation of holes in gold films for strong nonlinearities (that is, the long-range interactions are only weakly modified by a thin chromium layer) and undulation patterns if the strong attraction of the van der Waals forces, especially



**Shifting shapes**. Different morphologies exhibited by unstable thin polymer films. (Left) Polydimethylsiloxane film under water on a silicon substrate covered with a layer of end-grafted identical molecules. (Middle and right) An early and a late stage of dewetting of high molecular weight polystyrene on nonwettable silicon substrates. None of these states represents an equilibrium situation that would be isolated droplets. Images are 200 µm by 200 µm. Lighter colors represent thicker sections of the sample.

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close to the substrate, is "softened" by steric effects due to the structure of the liquid crystalline molecules. From the morphologies visible on a micrometer scale, together with knowledge about film thicknesses, they extracted the form of the interaction profile on a nanometer scale. They thus were able to infer the intermolecular interactions acting in their films just by looking through a microscope. These experimental findings are also in accordance with three-dimensional numerical simulations (10). Unfortunately, it is still not clear what kind of alternative process is able to produce in polystyrene films almost the same patterns found in gold films. Only a thorough analysis of the hole patterns based on Minkowski measures reveals differences, but it does not explain where they come from.

Why is an experimental proof of spinodal dewetting in thin films of so much importance? Because its existence implies that long-range forces over the distance of many molecular diameters can create patterns on macroscopic length scales. Furthermore, this process is an intrinsic phenomenon that can hardly be avoided without changing the system. Recent experiments show that these forces can be sufficiently strong to even destabilize thin liquid films confined between two solid walls, where one wall consists of a thin solid film. Thus, for many applications involving thin films or, in a more general sense, two parallel interfaces separated by some medium, the understanding and the control of the relevant molecular interactions are highly desirable.

What are the prospects for such control? The influence of ubiquitous longrange dispersive forces at separation distances up to 100 nm and more can be drastic, although these forces are, at such distances, already rather weak. This is largely neglected because directly at a surface or an interface they are mostly weak compared with specific interaction of short range. For example, long-range van der Waals forces (per unit area) at a distance of 100 nm amount to less than 1 Pa. Nonetheless, they can rupture 100-nm films, even if these films are "glued" to the substrate by specific short-range interactions. Experiments by Herminghaus et al. and others (1, 7) show that it is not possible to avoid such instabilities by a simple surface treatment or surface modification of the substrate. Improving adhesion between substrate and film by grafting polymers onto the substrate or by adding a thin layer of adhesion promoter [such as the chromium layer used by Herminghaus et al. (1)] will only stabilize films that are sufficiently thin, namely, about the thickness of this additional layer. Thus, we may be forced to reconsider the influence of long-range forces, especially at large separations, in areas ranging from physical properties of thin films (where processes

like phase transitions or phase separation differ from the behavior in the bulk) to biology (cell adhesion or deformation).

So, if one cannot avoid this problem, can it be of potential use? As indicated by Herminghaus *et al.* (1), we can learn about the intermolecular forces in films confined by a liquid-fluid interface. At present, especially for strong attractive forces. there are no other techniques available that have such a possibility. One may also consider using this creative power of intermolecular forces to produce regular patterns, probably by employing some lateral confinement in competition with the thickness-dependent characteristic wavelength of the instability. Structuring of multilayer systems by some intermediate unstable liquid layer seems also possible. Consequently, I expect that many groups will intensify their efforts in these directions and not just because of the aesthetic aspects of the evolving patterns.

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## PERSPECTIVES: EVOLUTIONARY GENETICS

# The Causes of Haldane's Rule

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Speciation, the splitting of single evolutionary lineages into reproductively isolated groups, remains one of the most elusive phenomena in evolution. The process requires thousands to millions of years, and we are confronted with a vast array of demonstrable contributors—geo-

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graphical isolation, natural selection, sexual selection, and changes in

karyotype, to name several—whose relative importance is difficult to untangle (1). The last 10 years have brought noticeable progress in the genetics of speciation progress that has come because evolutionary geneticists have focused largely on one aspect of speciation: the production of inviable and sterile hybrids and Haldane's rule. The most tantalizing regularity in animal speciation, this rule derives from Haldane's (2) observation that "When in the  $F_1$  [first generation] offspring of two different animal races one sex is absent, rare, or sterile, that sex is the heterozygous [heterogametic; XY, XO, or ZW] sex." Haldane's rule is a way station through which almost all pairs of animal species pass on their way to producing completely inviable or sterile hybrids (1). In a study on page 952 of this issue, Presgraves and Orr (3) provide neardefinitive data that address the causes of Haldane's rule. Contrary to the classic Popperian formula in which science marches forward over the corpses of rejected hypotheses, their report provides empirical support for both of the most widely accepted explanations.

Haldane's rule holds for 99% of 223 cases of sex-specific hybrid sterility and 90% of 115 cases of sex-specific hybrid inviability (3, 4) (see the figure). If stretched

to include cases in which hybrid females and males differ only quantitatively in fertility or viability, the rule extends to even more animals (4) and some dioecious plants (5). Its generality suggests that a common evolutionary force may underlie speciation in many different groups. The fact that Haldane's rule predicts inviable or sterile (heterogametic) males in Diptera and mammals, but inviable or sterile (heterogametic) females in Lepidoptera and birds, implies a critical role for the sex chromosomes in this intermediate step in speciation, rather than just for gender per se.

For more than 40 years, most evolutionists accepted an X chromosome–based explanation of Haldane's rule proposed by Muller (6). Muller's hypothesis built on Dobzhansky's (7) insight that genetic changes beneficial or harmless in one genetic background may be deleterious in another genetic background, because of negative interactions that had not been screened by natural selection. Thus, over time—on the order of  $10^5$  to  $10^6$  years—isolated populations accumulate increasing numbers of genetic changes that may be advantageous or neutral within species but that produce

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