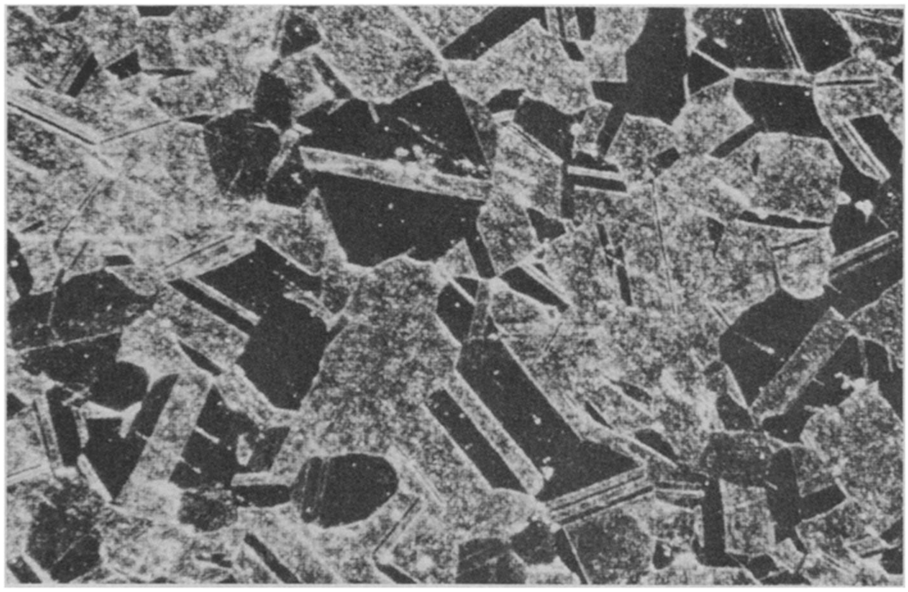
A METAL'S MANY FACES

A new mathematics helps elucidate how metals are put together

By IVARS PETERSON

A metal's etched surface typically shows a jumble of grains jammed together. This grain structure is a natural result of crystal growth. Each grain is a single crystal, made up of atoms in orderly arrays. When the metal solidifies, microscopic crystals that form within the liquid grow until they bump into their neighbors. The subtle interplay between physical forces and the geometric requirements of filling space sets the final grain boundaries.

In many cases, a metal's grain structure looks a lot like a soap froth, and sometimes it behaves like one. Steel, for instance, is a mixture of carbides and iron. When steel is heated up, grain boundaries shift. The grains act much like bubbles clustered together, where larger bubbles grow at the expense of smaller ones to create a coarser pattern.



The etched surface of a piece of brass, a mixture of copper and zinc, clearly shows the alloy's crystal structure. Each grain seen in the photo is a single crystal.

Such observations have led metallurgists to use soap froths as a rough model for a metal's grain structure. The model helps them understand the behavior of metals and suggests ways of manipulating grain structure to get metals with the right properties. "The manipulation of microstructure," says materials scientist John W. Cahn of the National Bureau of Standards in Gaithersburg, Md., "is an important, central feature of modern materials science."

But crystals aren't really like soap bubbles. Crystal surfaces lack the flexibility of soap films. They don't readily bend around corners. Instead, these surfaces tend to be flat and take on definite directions. This rigidity affects grain boundaries in ways that are not accounted for by the soap bubble analogy. "This is a complexity that we as metallurgists aren't taught to handle," says Cahn.

To get a better idea of the types of boundaries that can form between adjacent crystals, Cahn turned to mathematician Jean E. Taylor of Rutgers University in New Brunswick, N.J. More than a decade ago, Taylor, along with Frederick J. Almgren Jr. of Princeton (N.J.) University, had developed a simple mathematical model that accounts for why the many possible configurations of soap-bubble clusters are governed by only a few elementary rules (SN: 9/20/75, p. 186). Since then, Taylor has been extending her model to what, in effect, are cubic or polyhedral bubbles — forms that have well-defined faces. That's just the kind of mathematics that might apply to crystalline grains in metals.

The collaboration between Cahn and Taylor has now led to a catalog of the different interfaces that may occur between a crystal and a surrounding medium, whether solid, liquid or gas. Although their catalog is merely a first step and covers only one type of interface, the findings already suggest that some geometries, which metallurgists believed were caused by crystal defects, are actually forms that arise naturally in crystal growth within a solidifying metal. Their catalog was published last year in ACTA METALLURGICA (Vol. 34, p. 1).

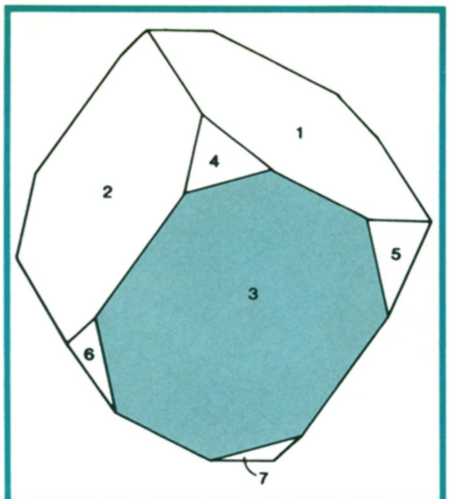
A soap bubble's shape is governed by surface tension, which is uniform over the whole bubble. An elastic soap film enclosing a parcel of air stretches only as far as it must to balance the air pressure inside.

The bubble is spherical because a sphere has the least possible area for the volume it encloses. A larger area would mean stretching the film and proportionately increasing its surface energy. Hence, a soap bubble's spherical shape minimizes the bubble's surface energy.

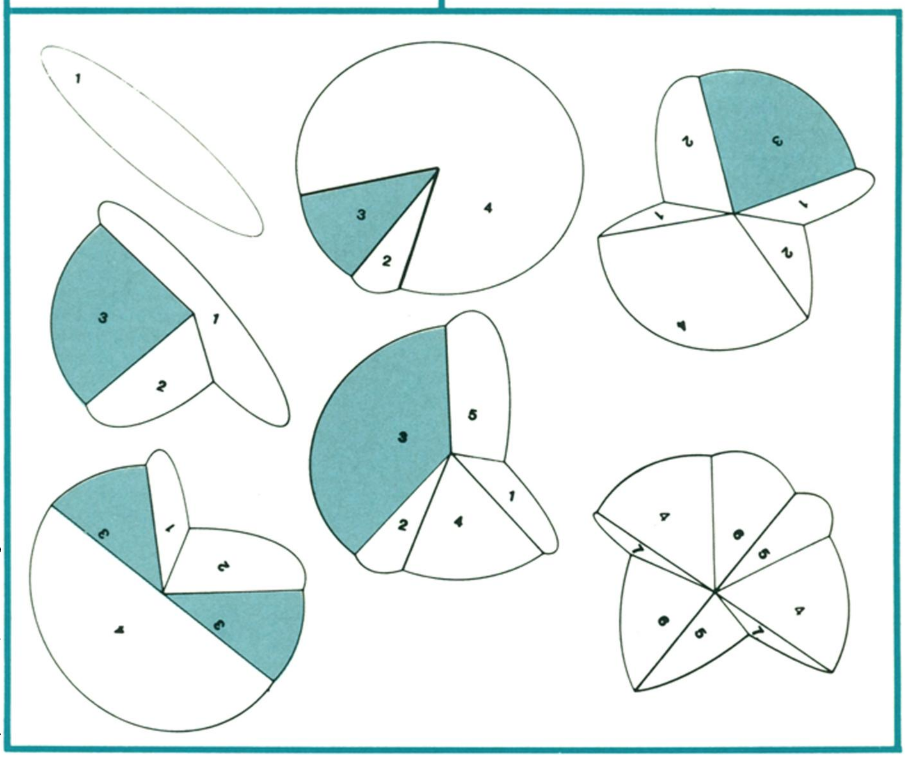
The principle of minimizing surface energy also determines the boundaries between crystals or between a crystal and a surrounding fluid. In the case of crystals, the surface energy value depends on the nature of chemical bonds left dangling at particular surfaces. The energy required to break apart a crystal may be much lower in some directions than in others. In that case, a crystal's surface energy would be anisotropic, varying from face to face.

Just as a sphere is the equilibrium shape of a single soap bubble, there is an analogous shape for anisotropic crystals. That unique shape would have the least total surface energy for a given enclosed volume. This special form, the anisotropic analog of a sphere, is often called the Wulff shape, named for crystallographer Georg Wulff, who suggested the idea in 1901.

Moreover, whereas soap bubbles and liquid droplets are all spherical (at least in the absence of gravity and other outside influences), crystals with different chemical compositions may have widely varying surface energy distributions and, therefore, different Wulff shapes. Depending on the material, these Wulff shapes may have the form of a cylinder, a cube, an octahedron or some other polyhedron. This implies that the equilibrium shape of a single crystal surrounded by a fluid or jammed against other crystals may be a polyhedron rather than a ball.



Taylor and Kahn chose a truncated cube (left) as the Wulff shape for their catalog of least-energy surfaces. Some examples from their catalog are shown below. In each case, Taylor and Kahn define a boundary enclosing a certain region or portion of the Wulff shape. If that region, for example, happens to lie entirely within one face, then the surface of least surface energy is a disk. Other placements of the boundary produce more complicated, three-dimensional combinations of surfaces. Altogether, the researchers found 12 distinct types of interfaces. The numbers on each "wedge" within the catalog of shapes correspond to the numbers on the faces of the Wulff shape.



Taylor and Kahn/© 1986 Pergamon Press

When two soap bubbles are brought together, each bubble keeps its spherical shape until the instant they touch. Once the bubbles touch, the films flow together, eliminating part of the outer surface of each bubble. This reduction in film area decreases the total surface area and energy of the original configuration. If the bubbles are of equal size, the interface is flat. If one bubble is larger than the other, the boundary film is a smooth curve that bulges toward the larger bubble.

In general, according to the principle of surface energy minimization, only three things can happen locally when soap films meet, even in large bubble clusters. First, a smooth sheet of film can separate space into two regions, as shown when two bubbles are brought together. Second, three sheets can meet at an angle of 120°. This occurs, for example, when three bubbles are brought together. Finally, six sheets can meet, three at a time along four edges that come together in a point. That configuration appears when a fourth bubble is placed atop a triangle of three bubbles so that the whole arrangement looks like a tetrahedron.

The analogous minimal structures for interfaces between anisotropic surfaces aren't completely known, says Taylor. As a first step, she and Cahn studied, classified and catalogued what can happen when an anisotropic surface has a given boundary. In other words, they looked at the analog of a soap film on a wire frame. Their approach involved isolating part of a larger interface in order to determine what types of local structures have minimal surface energies.

Taylor and Cahn worked with a Wulff shape in the form of a cube with lopped-off corners. This truncated cube, in various guises, covers most common crystal forms. For the truncated cube, they found 12 possible types of structures that locally minimize surface energy when an interface separates two regions. In contrast, for soap bubbles and isotropic surfaces in general, only a planar interface is possible.

"Many of these interfaces," says Taylor, "were not previously known to be possible, and the proof of their minimality corrects a number of misconceptions previously held and expressed in the [metallurgical] literature." She adds, "There is always the question of why the microstructure of a given material is as it is, and this catalog should settle one aspect of that question."

"What's happened," says Cahn, "is that a field that we thought was well understood has suddenly developed a new richness. We had seen all kinds of weird things in metallurgy, but we hadn't appreciated what we had seen."

In subsequent work, Taylor and Cahn also discovered a cusp-shaped singularity, at which a surface abruptly changes direction, yet its surface energy is still minimized. One cusp of this type looks like a ledge that peters out as it runs along halfway up a vertical wall. Such cusps have actually been seen on crystal surfaces, but metallurgists have usually interpreted them as the result of defects or nonequilibrium crystal growth.

Taylor and Cahn proved mathematically that a surface of least surface energy can contain a cusp. The presence of a cusp on a crystal surface, they suggest, need not imply that there is a dislocation in the body of the crystal or that the surface is not at equilibrium. They predict that these cusps can occur in crystals under equilibrium conditions. These findings were reported in SCIENCE (Vol. 233, p. 548).

Taylor's mathematical contribution goes well beyond applications in metallurgy. "She had to discover a new mathematics," says Cahn. "It's turned out to be a very beautiful and very elegant mathematics."

Taylor's foray into "cubic" bubbles and related anisotropic forms is an extension of centuries of research done on minimal surfaces, as inspired by soap film studies. The same questions that apply to soap films, says Taylor, can be asked for anisotropic surfaces.

"Except that most of the questions aren't answered yet," she adds. "There is much more unknown than known in this field." □