

Towards understanding snowflakes

The reasons why the microscopic anisotropy of molecules in crystals is reflected in the shapes of the macroscopic structures which they form have been obscure. Now there is some progress.

THE celebrated symmetrical hexagonal dendritic shapes of snowflakes are so familiar that they should long ago have been explained; that might be everybody's reasonable expectation. But the physics of the problem is not nearly as simple as it seems. The essential difficulty is to account for the way in which anisotropy on the scale of molecules is reflected in the shapes of macroscopic crystals.

The problem is not especially difficult with crystals that form a reasonably compact mass. The crystals grown by the multitude in kindergarten classrooms by suspending a crystal seed by a piece of thread in a supersaturated solution form in regular shapes for energetic reasons, because that is how best to minimize the free energy of the system; provided that the access of extra molecules (or ions) is equally easy from all directions, which requires that in practice the crystal seed should not be too close to the side of the jar in which it is suspended, extra elements will be added in such a way as to form sheets parallel to the planes in the basic unit cell. If access is not independent of direction, the result will be a misshapen crystal, but the underlying symmetry will remain at the level of the unit cell.

Dendritic structures such as snowflakes are more difficult because they combine what often seems a startling gross symmetry with a disconcerting disorderliness on the scale of the dendrites. The simple-minded rules of crystal growth seem not to apply. The article by Johann Nittmann and H. Eugene Stanley (this issue, p.663) goes a long way to explain why some recent attempts at a solution have not succeeded fully. More than that, it embodies the essence of an explanation of the growth of dendritic crystals.

Broadly speaking, there have been two complementary approaches to the problem, the first due to J.S. Langer (reviewed by Langer in *Rev. mod. Phys.* **82**, 1, 1980), who has dealt with the growth of dendritic tips by the diffusion of new material through the surrounding medium. The arguments apply as well to crystallization from a solution as to condensation from a vapour phase. The rate at which material is added to a particular point on a growing surface is determined by the local geometry in the sense that protuberances are more likely than re-entry points to acquire material by diffusion. There may be circumstances in which growth is limited by the need that latent heat should be con-

ducted away from the surface. The fact that growth depletes the local environment of the uncondensed phase of material means that growth will also be limited by the rate of diffusion. The usual upshot is a set of differential equations that cannot usually be solved exactly, but can be used to define the conditions under which a dendritic tip will continue to elongate or, alternatively, split.

The frustrations of this approach have stimulated the more recent phase of computer simulation, of which T.A. Witten was the first exponent (see Witten, T.A. & Sander, L.M. *Phys. Rev. Lett.* **47**, 1400; 1981). In the simplest model of diffusion-limited aggregation, as it is called, extra elements of the material of which a crystal is being constructed are supposed to be added to the system at random points of some distant boundary and are allowed to migrate by means of a random walk along the links of some underlying lattice. If the diffusing element should reach a point on the lattice which is an immediate neighbour of the growing aggregate, it may be supposed captured, but there are a host of ways of defining the aggregation rules, most of which appear to have been tried in the past few years.

The virtue of these simulations is that they yield patterns which indeed resemble those of real aggregates. In particular, they show that aggregates whose growth is limited by diffusion are fractal structures; in two dimensions, for example, the number of elements in an aggregate is not proportional to the square of its dimensions but to some lesser power of them, called the fractal dimension. At some cost in computer time, the simulations can be (and have been) carried out in any number of dimensions.

What Nittmann and Stanley have done is to combine these two approaches or, more accurately, to carry out lattice-based simulations of aggregation in a way that can be made to correspond to equations of the kind that Langer (and, now, many others) formulated. They have overcome the persistently annoying feature of simulations, the difficulty of telling the meaning underlying the patterns produced, by producing a series of patterns corresponding to the variation of some physical parameter over a known range. Their aggregation rules are among the simplest there could be, consisting simply of the requirements that new elements are added at random to the periphery of a growing

aggregate, but that their assignment to the sites available is biased to reflect what the macroscopic equations suggest will be the rate of growth there.

One result of consequence to emerge arises from the fact that the simulation model can deal only with the addition of discrete elements to the aggregate. There are, as a consequence, departures from the macroscopic prediction of the regular outward extension of a regular envelope of the growing aggregate, which is fairly described by the authors as noise. The essence of this part of the result is that outward extensions of the surface are quickly smoothed out by the later addition of material, but that inward depressions are less readily filled in, but may instead persist as the apices of what are to become fiords in the pattern as the aggregate grows.

The simulations (see p.664) show that the patterns are typically broken up into a number of radially extended tongues of substance separated by lengthening fiords, while the tips of new fiords repeatedly form at the outer surfaces of the extending tongues. Given that the aggregation rules correspond to the penetration of one liquid into another with which it is immiscible, it is pleasing but not surprising that the fractal patterns formed resemble those found in such experiments. The circumstances correspond to those of practical importance in which oil companies pump water down into the oil wells so as to displace crude oil from its reservoirs.

But the most remarkable result of these simulations stems from the apparently successful attempt to allow for the anisotropy of the real world, which depends on the assumption that not all sites on the surface of a growing aggregate are equally suitable energetically. The criteria used in extending the aggregation rules are strictly microscopic; they depend only on the orientation — some sites are more likely to be occupied than their immediate neighbours.

One outcome is the pattern of an aggregate which is virtually indistinguishable from a fairy-tale snowflake, a feathery collection of dendrites which is plainly hexagonally symmetric overall, but whose smaller-scale structure is far from symmetric, which is the case with real snowflakes. That looks a convincing demonstration that the snowflake problem is on the way to solution. **John Maddox**