Crystal Anisotropy and Dendritic Crystal Growth

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Abstract

Observation of selected low-symmetry crystals growing in the dendritic morphology indicates the importance of crystal structure in determining not only the sidebranch spacing but also the very existence of sidebranching. This evidence provides a perspective which supplements the view of sidebranching as being governed by the continuum dynamics of a moving solid–liquid interface. Direct evidence is presented for a parabolic diffusion field surrounding growing dendrite tips. The existence of this field is consistent with the theoretical analysis which leads to the needle-crystal model of dendritic growth.

Introduction

The growth of crystals in the dendritic (treelike) morphology is a departure from the usual idealized polyhedral shapes visualized and sought by crystallographers. The two most apparent features of dendritic crystals, compared with normal convex polyhedral morphologies, are the formation of elongated spikes in particular directions and the development of sidebranches on several smaller length scales, so that the idealized shape is fractal (Nittmann & Stanley, 1986). Fig. 1 shows a computer-generated fractal with a shape similar to that of NH_4Cl dendrites; the Hausdorff–Besikovitch (fractal) dimension is 1.45. The fractal model is a useful way to visualize a dendritic crystal at any particular instant in its growth. However, Xiao, Iwan, Alexander & Rosenberger (1988) have shown that the fractal dimension of a growing dendrite changes as the dendrite gets larger, so that actual crystal dendrites may not have the rigorous scale-invariance of objects such as diffusion-limited aggregates.

Much recent effort at understanding the origin of dendritic morphology has been based on dynamical models. Over the past decade, dynamical models have been developed with considerable rigor, as exemplified by the work of Langer (1986), Ben-Jacob, Goldenfeld, Langer & Schön (1984) and Brower, Kessler, Koplik & Levine (1983). In this approach, one starts with some variation of the fundamental continuum diffusion equations governing either heat diffusion away from a crystal growing from the melt or solute diffusion toward a crystal growing from solution. When appropriate boundary conditions are imposed, such models yield solutions suggesting a moving parabolic interface consistent with tip-shape observations on various dendritic crystals, including succinonitrile (Huang & Glicksman, 1981), ammonium bromide (Dougherty, Kaplan & Gollub, 1987) and ammonium chloride (Honjo, Ohta & Sawada, 1985). This 'needle crystal' has been a central theme of the dynamical approach and agrees well with experimental observations of the growing tip of a dendritic crystal. That the sidebranching characteristic of dendritic crystals is less well understood has been discussed by Dougherty, Kaplan & Gollub (1987) and by Caroli, Caroli, Roulet & Langer (1986). Computer simulations based on dynamical models have produced structures with sidebranching, but this is accomplished by building in a periodic 'anisotropy function' (Saito, Goldbeck-Wood & Müller-Krumbhaar, 1987).
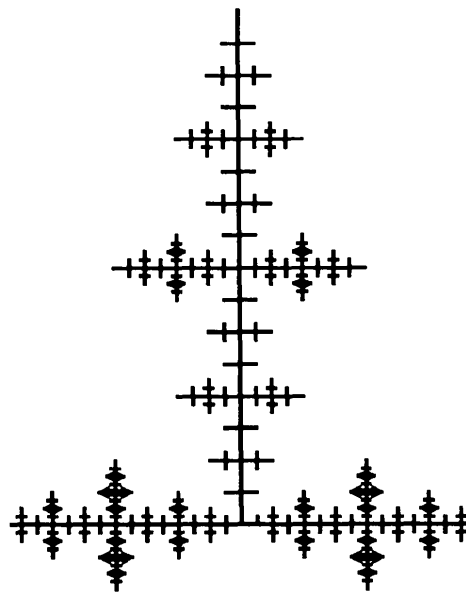

Fig. 1. Computer-generated dendritic fractal. Hausdorff-Besikovitch dimension $D = 1.45$. Compare with Fig. 4. (Figure produced with FractaSketch, Dynamic Software, Santa Cruz, CA, USA. This program generates fractals using a self-similarity transformation.)

In the present work, we emphasize the role of local crystallographic effects in determining the morphology of dendritic crystals. Earlier theoretical work based on growth mechanisms at the crystal surface, such as the discussion of Sunagawa (1981), seems more directly in accord with our findings. It seems likely that the dynamical viewpoint will be be useful in understanding those aspects of dendrite formation that can be perceived from afar (a viewpoint from which the interface looks continuous), while the mechanistic view will be useful for understanding morphological details and differences in dendritic habit among various substances.

Experimental

Dendritic crystals of the chosen materials were grown from aqueous solution by cooling. Observation chambers were prepared by mounting a microscope coverslip on a bead of silicone sealant on a microscope slide. The first bead was positioned so that it would seal three sides of the coverslip. A spacer was held under the coverslip while the coverslip was being pressed into place on the bead, giving approximate control over the chamber depth; the depth used in the work reported here was 0.1 mm. Then, a sample of the desired solution, saturated at an elevated temperature, was introduced into the chamber and the fourth side of the coverslip was sealed with a silicone bead.

At the start of an experiment, the sealed slide was held at the desired starting temperature (below the original mounting temperature) so that the solution in the chamber was saturated at the thermostat temperature. Then, the slide was quickly transferred to a temperature-controlled stage mounted on a Vickers M72 microscope that was equipped with a video camera and a four-head video recorder. In this manner, the supersaturation prevailing during the initial stages of dendrite growth could be controlled by regulating the difference in temperature, ΔT, between the thermostat and the microscope stage. A similar method has been employed by Dougherty, Kaplan & Gollub (1987); those authors compute a dimensionless supercooling, $\Delta = (C_\infty - C_{eq})/(C_s - C_{eq})$, where C_∞ is the concentration of the high-temperature saturated solution before cooling, C_{eq} is the equilibrium concentration of the solution at the low temperature at which the crystal is growing and C_s is the 'concentration' of the solid. This method permits easier control of the initial growth rate compared with observations on growth from the melt, where temperature variations of a few hundredths of a degree affect the character of the dendrites. The disadvantage, of course, is that the supersaturation decreases as the growing crystal advances, so that only the initial period of dendrite growth is characteristic of the measured ΔT.

Frames from video tapes of the growing dendrites were captured with an IBM PC-AT computer equipped with a frame grabber and, in some cases, subjected to contrast enhancement to bring out features of interest.

For study of the diffusion field around the growing dendrites, the microscope was outfitted with a Vickers 10× shearing interference objective and matching condenser. This double-beam optical system superimposes an image of the object of interest upon a reference image of the unoccupied field 330 μm from the object. The light forming these two superimposed images is coherent, so any path difference between the two images produces a characteristic interference color. In the present case, the 'object of interest' is the region immediately surrounding the dendrite tip and the 'unoccupied field' represents solution as yet unperturbed by the growth of the crystal. In this manner, refractive-index variations in the solution around the growing crystal are made visible. Growth sequences imaged with this optical system were recorded and processed as described above.

Results and discussion

Lithium chloride

From aqueous solution, LiCl crystallizes in a series of hydrates, from the monohydrate to the pentahydrate. The anhydrous salt crystallizes only above 373 K (Sneed & Brasted, 1957). We have grown lithium chloride dendrites by supercooling from 328 to 293 K, a temperature region where only the monohydrate is stable. For the conditions under which we have grown $LiCl.H_2O$ dendrites, Jacobi (1972) has shown that the crystals are orthorhombic and tend to grow as vierlings (four-component twins) which twin on the (101) and (10$\bar{1}$) planes. The sutures at the twin plane are visible in Fig. 2 as a line along the long axis of the dendrite leaf. In most, though not all $LiCl.H_2O$ dendrites, there is a marked difference in the sidebranch wavelength on opposite sides of this suture (see Fig. 2). [The terms 'wavelength' or 'frequency' are used in connection with dendrites as a measure of the periodicity of the sidebranching. Dougherty, Kaplan & Gollub (1987) have shown that the power spectrum of the sidebranching pattern typically contains one or more characteristic peaks.]

The importance of crystallographic orientation in determining dendrite morphology is particularly clear in the case of $LiCl.H_2O$. In a typical $LiCl.H_2O$ dendrite, the opposite sides of the leaf are in such close proximity that there can be no important difference in the environment to which they are subjected. However, because of the twinning, the opposite sides differ crystallographically. The large difference in sidebranching wavelength must be due to the

difference in the crystal planes from which the side-branches emanate. Furthermore, on the long-wavelength side of the dendrite, the sidebranches originate well behind the growing tip. This suggests that the sidebranch genesis is not related to any motion of the tip itself, a conclusion which Dougherty, Kaplan & Gollub (1987) reached for different reasons.

Examination of the $LiCl.H_2O$ dendrite in Fig. 2 reveals faceting. Sunagawa (1981) and Xiao, Iwan, Alexander & Rosenberger (1988) have examined the transition from faceted to dendritic growth, the former with actual crystals and the latter using a Monte Carlo model. In both cases, the supersaturation is a key parameter. The faceting seen in our dendrites may be due to later growth at lower supersaturation well behind the main tip.

Ammonium nitrate

Ammonium nitrate is polymorphic, crystallizing in five different crystal structures at atmospheric pressure (*Crystal Data*, 1973). Between 305 and 357 K, orthorhombic NH_4NO_3 (III) is stable; the space
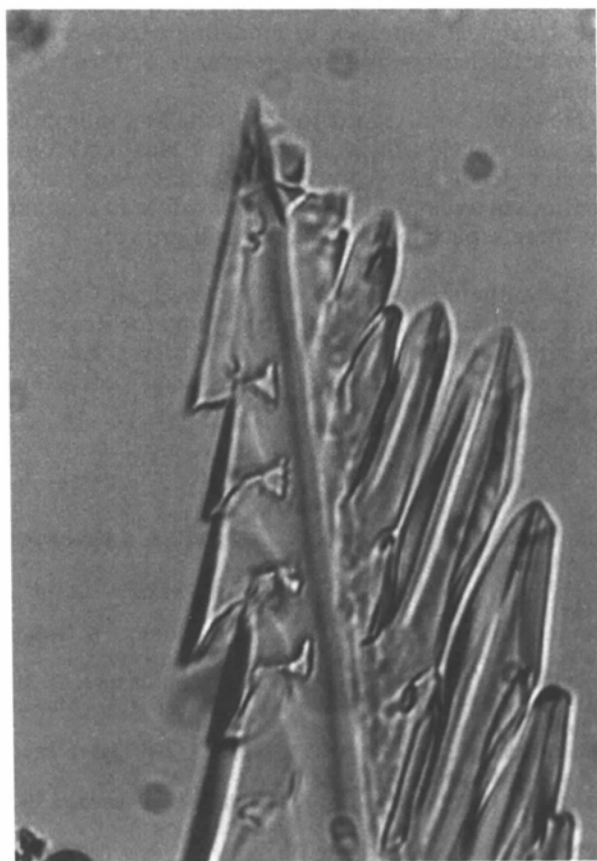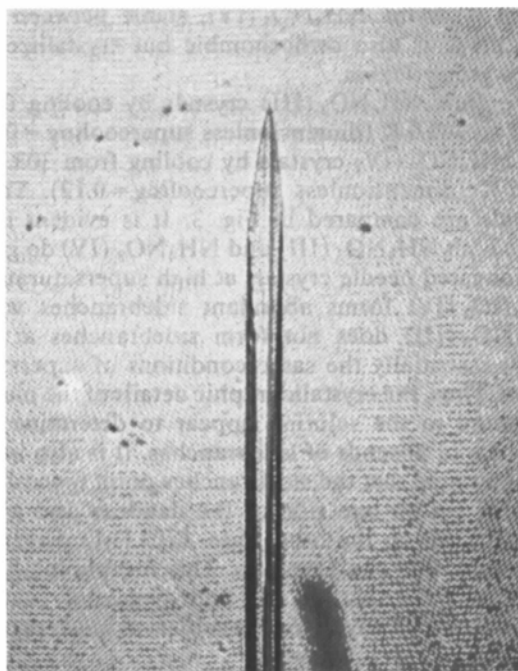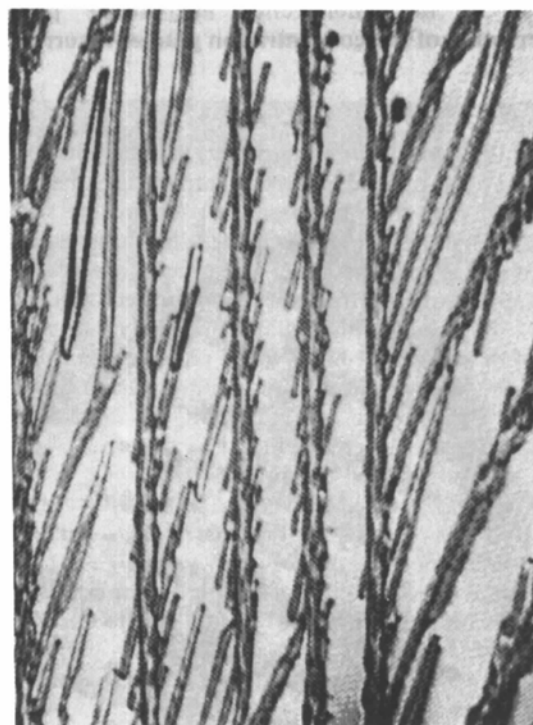
(a)

Fig. 2. $LiCl.H_2O$ dendrite, grown by supercooling from 328.1 to 293.1 K. Dimensionless supercooling $\Delta = 0.022$. Undigitized image. Height of photograph represents 0.23 mm.

(b)

Fig. 3. (a) NH_4NO_3 (III) dendrite, grown by supercooling from 318.1 to 308.0 K. Dimensionless supercooling $\Delta = 0.14$. Digitized image. Height of photograph represents 1.2 mm. (b) NH_4NO_3 (IV) dendrite, grown by supercooling from 303.6 to 294.7 K. Dimensionless supercooling $\Delta = 0.12$. Digitized image. Height of photograph represents 1.2 mm.

group is *Pbnm*. NH_4NO_3 (IV), stable between 255 and 305 K is also orthorhombic but crystallizes in space group *Pmmn*.

We grew NH_4NO_3 (III) crystals by cooling from 318.1 to 308.0 K (dimensionless supercooling = 0.14) and NH_4NO_3 (IV) crystals by cooling from 303.6 to 294.7 K (dimensionless supercooling = 0.12). These crystals are compared in Fig. 3. It is evident that, while both NH_4NO_3 (III) and NH_4NO_3 (IV) do grow as elongated needle crystals at high supersaturation, NH_4NO_3 (IV) forms abundant sidebranches while NH_4NO_3 (III) does not form sidebranches at all, under essentially the same conditions of supersaturation. Thus, the crystallographic details of the planes presented to the solution appear to determine the presence or absence of sidebranches. It is also interesting to note that the sidebranches point toward the growing tip on one side of the dendrite and away from the tip on the other side. $LiCl.H_2O$ dendrites also show this characteristic. This morpholology is different from that of the high-symmetry (cubic) materials which have been the subject of much experimental work on dendrites.

Interference microscopy

Use of the interference microscope permits observation of the concentration gradients surround-
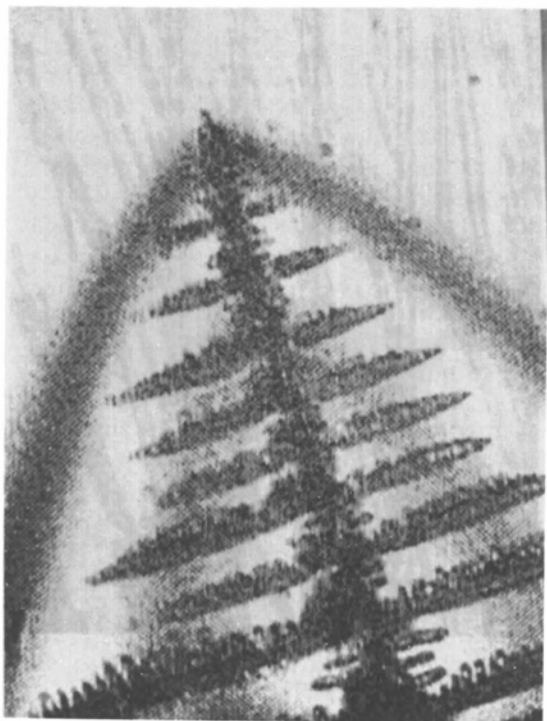

Fig. 4. NH_4Cl dendrite, grown by supercooling from 310.1 to 293.1 K. Dimensionless supercooling $\Delta = 0.050$. Double-beam interference optics. Digitized image. Height of photograph represents 0.72 mm.

ing the growing crystals. Fig. 4 shows a typical interference image of a dendrite of NH_4Cl, the direction of elongation being [100]. The parabolic shape of the outermost interference fringe is noteworthy; digitized photographs of the fringes, fit with a least-squares curve, confirm the parabolic shape. The lateral extent of the fringe pattern is also significant, as it corresponds closely to what would be expected for mass diffusion but is about eight times narrower than would be expected for thermal diffusion (Ohsaka & Trinh, 1988).

Summary

The dynamical view of dendritic crystal growth associates this phenomenon with far-from-equilibrium processes. This perspective has much to recommend it. A dendritic crystal cannot be an equilibrium structure, since it must have a higher free energy at the surface than a compact simple polyhedral crystal of the same volume. Indeed, the sidebranches of solution-grown NH_4Cl dendrites become constricted at their bases and separate from their points of attachment within a few minutes of the cessation of growth (Soltzberg, Hidek & O'Brien, 1990). The success of the dynamical approach in modeling needle-crystal growth further supports the relevance of this viewpoint.

However, with regard to sidebranching morphology and wavelength, it appears that local crystallographic details have so profound an influence that a continuum dynamical view will not suffice to account for these aspects of dendritic crystal growth.

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Topological Approach to the Niggli Lattice Characters

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Abstract

The way in which Niggli characters are introduced nowadays is not very satisfying. In this paper a more exact abstract method based on topological concepts is proposed. Any lattice can be represented by a point in E_5, its Niggli point. Then to any system of lattices there corresponds a set of points in E_5 called the image of this system. A Bravais type is taken formally as a system of all lattices of this type. The same can be done with the Niggli characters. The main result is: The image of a Niggli character is a component (*i.e.* a maximum connected subset) of the image of that Bravais type which contains the character. The image of any Niggli character is a convex set. This enables a simple physical (dynamical) interpretation. Since the decomposition of a set in E_5 into components is unique it can be used conversely for definition of the Niggli characters.

Introduction

The Niggli lattice characters* (Niggli, 1928; Mighell, Santoro & Donnay, 1969; de Wolff, 1983) are used to introduce a finer division of lattices than the commonly used Bravais types. It is not the only attempt that has been made. Most readers are acquainted with the method of Delaunay (1933) used in the old editions of *International Tables for X-ray Crystallography* (1952) for determining the Bravais type of a lattice. The criterion here is the shape of the Voronoi domain. The table constructed by Delaunay distinguishes 24 cases giving a division of lattices into 24 *Sym-*

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* Also called 'lattice characters' or 'Niggli characters' or simply 'characters'.

metriesorten. This is a subdivision of the Bravais types, the *hR, tI, oI* and *mI* lattices being further divided according to special relations between the parameters of their conventional cells. The Delaunay procedure is elegant though not very quick and has experienced a revival thanks to Burzlaff & Zimmermann (1985) who have written a computer program *DELOS* (Zimmermann & Burzlaff, 1985) which is based on this procedure.

From a quite different angle the problem has been studied by Schwarzenberger (1972). His approach is abstract and requires a considerable knowledge of topology. In principle (and in short), he works with the sets of all lattices, all primitive bases and all reduced bases making them (after some identifications) topological spaces. This is done by means of a map from the general linear group. General considerations are carried out in n dimensions and detailed results gained for $n = 1, 2, 3$. They are illustrated by instructive figures. In this classification, the *tP, tI* and *oC* lattices are further divided.

The present *International Tables for Crystallography* (1987) use for determining the Bravais type a method suggested by Niggli (1928) which has its roots in the reduction theory of the positive-definite quadratic forms. It divides lattices into 44 classes called characters which can be described by special relations between the shortest vectors. Thus they are more freely related to the symmetry of the lattice, forming nevertheless a subdivision of the Bravais types.

Each of the three mentioned classifications is based on different principles. Therefore, their convenience and applicability to various tasks are different. It is not the aim of this paper to compare their particular advantages and disadvantages and to study their intrinsic relationships. Here we are interested only in one of these classifications, the Niggli characters.