THEORY OF SPHERULITIC CRYSTALLIZATION

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I show that diffusion-controlled growth can account for the occurrence of spherulites, their small-angle non-crystallographic branching, and the linear form of their radial growth rate. The characteristic dimension of the large-scale morphology is predicted to scale with $\sqrt{\delta}$, where δ is the diffusion length. These results provide quantitative support for the mechanism of spherulitic growth proposed by Keith and Padden.

1. Introduction

Spherulites are polycrystalline aggregates with an approximately radial symmetry. Close inspection reveals that they are comprised of a radiating array of crystalline fibres, which branch at small, non-crystallographic angles, giving rise to secondary fibres whose crystallographic orientation differs from that of the primary fibres. Successive generations of fibres repeatedly branch, apparently at random, to form a space-filling structure, whose diameter may be of the order of micrometres, or in some cases even larger. Spherulites are commonly formed by minerals crystallizing from viscous magmas and devitrified glasses, by high polymers crystallizing from the melt, and by organic compounds crystallizing from melts with added thickeners. In all of these cases, the melts are of relatively high viscosity and the crystallization is slow; furthermore, some degree of undercooling is invariably required.

Despite the wide diversity of physical and chemical properties among spherulite-forming melts, the growth and subsequent morphology are surprisingly universal. The morphology has been described above. About the growth little is known, apart from the observation that the radius $R(t)$ usually varies linearly with time t. An explanation of the existence of spherulitic growth should be independent of the fine details of each individual system, and should be based only on those features which are shared by all spherulite-forming melts.

Such an explanation was provided in a seminal paper by Keith and Padden [1] in 1963. Keith and Padden observed that spherulite-forming melts have the character of alloys rather than that of pure substances. Even in the case of polymer melts of a single species, there are polydisperse components of the melt, not to mention stereo-irregular components, which crystallize less readily than the majority component, and which will be rejected preferentially from the growing solid. I shall, in the following, refer to the rejected component of the system being considered by the term "impurity". The rejection of the impurity leads to an excess concentration of impurity which is pushed ahead of the growing crystal. Keith and Padden argued that this impurity boundary-layer was in some way responsible for the fibrillation observed in spherulites, although they were unable to give any precise arguments as to why this should be the case. The purpose of the present paper is to provide these arguments.

The core of these arguments is the newly-developed theory [2] for the motion of diffusion-controlled interfaces, which has been successfully applied to the problems of dendritic growth and viscous fingers in two-dimensional hydrodynamics. Until recently, it had been assumed that

dendritic crystallization was the signature of diffusion-controlled growth, and furthermore, that the qualitative features of the growth were determined solely by diffusion and surface tension [3]. It is currently believed that this traditional view is incorrect, and that crystalline anisotropy, arising from the presence of a crystal lattice, must also be included in order to explain the occurrence of dendritic growth. In the modern theory, and in experimental tests of the theory, a range of morphologies can result from the growth dynamics of the interface, as the driving force and anisotropy strength are varied. One of these morphologies – the dense branching morphology (DBM) [4] – is, I propose, the spherulitic structure which is the subject of this paper.

Since I shall be concerned with the different morphologies which may result from diffusion-controlled growth, it is appropriate to define carefully the terms *dendritic growth* and *dense branching morphology*. Dendrites are complex time-dependent solidification fronts. Under carefully controlled conditions, they exhibit a smooth, approximately parabolic tip, which propagates without apparent change of shape, followed by a train of oscillatory sidebranches with a well-defined periodicity. In the laboratory frame, the tip propagates at a constant velocity, whilst the sidebranches grow away from the main body of the dendrite. The sidebranches grow until they too become fully-developed dendrites, growing in crystallographically favoured directions away from the parent dendrite. In contrast to this dendritic morphology, the dense branching morphology is not the result of a steadily propagating tip. Instead, the advancing growth front repeatedly bifurcates, generating an apparently randomly branched structure with no obvious regularity. Although a distinction is sometimes not drawn between these two morphologies, they are quite different, as we shall see.

In section 2, I shall briefly review the theory of Keith and Padden, describing the quantitative predictions made, and focussing on the conceptual basis of the theory. Section 3 recalls the evidence for the view that crystalline anisotropy is of prime importance in understanding the dynamics of unstable interfaces, and summarizes the present understanding of diffusion-controlled interface motion. Section 4 shows how the Keith–Padden theory may be clarified and extended in the light of recent developments, and makes a crude prediction for the scaling of the characteristic length scale with the diffusion length, which differs from that originally given by Keith and Padden.

2. The theory of Keith and Padden

The theory starts from the assumption that during crystal growth, impurities are segregated from the crystal, thus forming a boundary-layer ahead of the solidification front. The hypothesis that growth is controlled by diffusion is discarded, as this would lead to a growth law of the form $R(t) \sim \sqrt{t}$, which is inconsistent with experiment. In addition, diffusion-controlled growth was believed to result in dendrites, a morphology quite different from spherulites. Thus, one is led to the conclusion that nucleation-controlled growth is a dominant feature of spherulitic growth. Keith and Padden proceed by showing how an instability of a planar interface akin to constitutional supercooling might lead to fibrillation. Let us rehearse this argument below. The concentration of impurities, C, in the solidified material may reasonably be taken as zero, whilst at a point x in the melt, the normalized concentration field, $u(x, t)$, satisfies the diffusion equation

$$D \, \nabla^2 u = \partial u / \partial t, \tag{2.1}$$

with boundary conditions at the interface

$$u_s = \Delta - d_0 \kappa, \tag{2.2}$$

$$v_n = -D \, \nabla u \cdot n. \tag{2.3}$$

Here,

$$u(x, t) = \frac{C(x, t) - C_\infty}{\Delta C}, \tag{2.4}$$

D is the impurity diffusion coefficient, v_n is the velocity of the solidification front along n, the outward normal to the solidification front; u_s corresponds to the impurity concentration at the solidification front, and κ is the curvature of the solidification front. The coefficients Δ and d_0 are,

respectively, the dimensionless supersaturation and the capillary length, given by

$$\Delta = \frac{C_{eq} - C_\infty}{\Delta C},\qquad (2.5)$$

$$d_0 = \frac{\gamma V C_{eq}}{\Delta C k_B T_m},\qquad (2.6)$$

where ΔC is the miscibility gap (assumed not to depend on κ), C_{eq} is the equilibrium concentration of impurity in the melt at the two-phase interface, C_∞ is the impurity concentration at infinity, γ is the surface tension, V is the atomic volume, T_m is the equilibrium melting temperature, and k_B is Boltzmann's constant. These equations are supplemented by the boundary condition at infinity that $u(x, t) \to 0$.

Eqs. (2.1)–(2.6) do not possess uniformly translating planar solutions except in the special case $\Delta = 1$. In general, the planar interface moves with a velocity, which for large times, scales like $v \sim t^{-1/2}$. In the special case $\Delta = 1$, or in the case of directional solidification, where material is pulled at constant velocity along the x-axis through a temperature gradient, steady state solutions exist, of the form

$$u(x, t) = \Delta \exp(-x/\delta),\qquad (2.7)$$

where the diffusion length, δ, is given by

$$\delta = D/v,\qquad (2.8)$$

and v is the a priori arbitrary velocity of the solidification front [3].

Constitutional supercooling provides a criterion for the onset of instability of the planar interface, eq. (2.7), in the cases of $\Delta = 1$ or directional solidification. In the case of isothermal solidification of an alloy, as considered by Keith and Padden, an analogous criterion exists, with the temperature field replaced by the impurity concentration field. This criterion predicts that the planar interface is unstable to the formation of cells whose characteristic width is of order δ. Keith and Padden interpret this result in the context of spherulitic growth. The imposed temperature gradient, in the case of directional solidification, presumably corresponds to the contraint provided by nucleation-controlled growth. The insta-

bility is then responsible for the fibrillation, and the characteristic size of the fibres (counterparts of cells), L_f, is then δ.

This is the crux of their theory. It is still controversial [5] as to whether or not experiment verifies the semi-quantitative prediction that the fibre size scales with δ; the issue seems to concern the interpretation of L_f. It will be clear from the discussion in the subsequent sections that L_f is not to be identified with the microstructure on the scale of lamellae. Instead, L_f is a length scale characteristic of the large-scale morphology, and describes a level of organization higher than that of the lamellae. This separation of length scales is clearly illustrated in fig. 1. The figure is a photograph of a spherulitic structure, formed by

Fig. 1. Spherulite of poly-(phenylene sulfide) grown from solution, clearly showing the presence of two distinct levels of organisation: a macroscopic morphology, and a microscopic, lamellar morphology. Figure by kind permission of H.D. Keith and F.J. Padden, Jr.

poly(phenylene sulfide), crystallized from solution. It is likely that the solution underwent phase separation, and that the displayed spherulite grew from a concentrated droplet; I show this figure for the purpose of illustration only. Clearly visible are stacks of lamellae, organized into lobes. It is the lobes, characteristic of the large-scale morphology, whose dimensions are described by the number L_f. The microstructure, as exemplified by the lamella spacing in the case of polymeric spherulites, is determined by the fine details of the crystallization process, and is not described by the theories considered in the present paper. Whatever the outcome of this debate, however, certain theoretical points require elaboration. Let us examine these points in the remainder of this section.

The first point to notice about the theory is that although diffusion-controlled growth is dismissed at an early stage, the final theory does indeed appeal to diffusion-controlled interface dynamics. The supposed nucleation-controlled character is included insofar as the steady state solution for planar interface growth is invoked. Thus, the theory, as it stands, is still open to the objection that it predicts that $R(t) \sim \sqrt{t}$, in apparent contrast to the experimental observations. We shall see in section 4 how this point may be dealt with.

Secondly, the weakest part of the theory is the prediction that the fibre dimensions scale linearly with δ. This prediction results from the use of ideas relating to constitutional supercooling. At about the same time that the Keith–Padden theory was proposed, Mullins and Sekerka [6] showed how the instability of diffusion-controlled interfaces is related to dynamics, not thermodynamics. In particular, they identified two competing influences operating on the interface, by performing a linearized stability analysis of the dynamics of the interface. The first influence is the destabilization of the interface due to diffusion, and was already recognized by Keith and Padden in their original paper. Any outwardly directed perturbation of an initially planar interface will cause the isotherms in the melt to cluster around the perturbation, thus increasing the local gradient, and causing the interface to grow even faster, by virtue of eq. (2.3). So perturbations tend to grow. This instability is weakened by the action of

the Gibbs–Thomson boundary condition, eq. (2.2) – the coupling between the surface temperature and the curvature of the interface. As the tip of the perturbation grows and becomes sharper, the curvature increases, and the impurity concentration drops there. Accordingly, more material diffuses to the tip, raising the concentration and causing the tip to flatten, by virtue of eq. (2.2). Thus, a planar, diffusion-controlled interface is unstable to long wavelength perturbations, but is stable to short wavelength perturbations. The length scale at which the two competing effects become equal in magnitude defines the stability length, λ_s, given by

$$\lambda_s = 2\pi\sqrt{d_0\delta} \ . \tag{2.9}$$

It is λ_s which confers the resulting pattern with a characteristic size, although this is still a very crude approximation owing to the linearized analysis. In section 4, I will argue that Keith and Padden's physical picture is indeed correct, but that quantitative predictions such as $L_f \sim \delta$ must be modified to be of the form $L_f \sim \lambda_s$.

The third comment is related to the origin of small-angle non-crystallographic branching. Keith and Padden attribute this to microscopic disorder at the interface (such as screw dislocations in the case of polymeric substances), but are unable to explain in a general way why such disorder might lead to the branching. For example, if the motion of the interface is controlled by diffusion, as the argument leading up to the prediction that $L_f \sim \delta$ suggests, why is dendritic growth not observed to occur? A partial answer to this is provided in section 4.

3. Dynamics of unstable interfaces

For many years, the formulation expressed by eqs. (2.1)–(2.6) was believed to encapsulate all the physics essential to account for dendritic growth. The advent of simplified models for diffusion-controlled interface dynamics [7] and interfacial pattern formation [8] permitted, for the first time, detailed numerical studies of the time-dependent behaviour of interfaces, well into the non-linear regime. The boundary-layer model (BLM), in par-

ticular, describes the dynamics of diffusion-controlled interfaces in the regime where the supersaturation Δ is sufficiently large that $\delta\kappa \ll 1$ at all points on the interface. In this regime, the diffusion can be assumed to be essentially curvilinear along the solidification front, and to take place within a thin boundary-layer whose thickness varies with position along the interface. The BLM has been shown [7] to be asymptotically close to the traditional formulation, eqs. (2.1)–(2.6), as $\Delta \to 1$.

In the numerical studies of the BLM, and in subsequent studies of pattern formation at interfaces, the following results were established [7,8]. The traditional formulation of diffusion-controlled growth, taking into account only the competition between diffusion and surface tension, is not sufficient to account for the existence of dendrites. With these two effects included only, the interface evolves by a sequence of instabilities which are graphically described as tip-splitting. Instead of evolving into a well-defined tip, propagating persistently in one direction in space, followed by a train of sidebranches, a potentially dendritic perturbation of the interface bifurcates and branches into two different directions in space. The branches then grow in size, until, when they are of the dimensions λ_s, they too bifurcate, and so on. Crystalline anisotropy was included in the model by allowing the capillary length, d_0, to be a function of θ, the angle between $\mathbf{n}$ and a specified crystallographic axis. The inclusion of this effect was shown to lead to dendritic-like growth. Crystalline anisotropy biases the instabilities of the interface to grow in preferred spatial directions, allowing the formation of coherent tip structures; thus crystalline anisotropy plays an essential role in the dynamics. Recently, it has also been shown that uniformly translating non-planar solutions of eqs. (2.1)–(2.6) do not exist in the absence of crystalline anisotropy, indicating that the anisotropy is essential for the formation of shape-preserving dendritic tips [10].

These theoretical results have also been demonstrated in experimental studies of the growth of bubbles in a Hele-Shaw cell [4,11]. A Hele-Shaw cell consists of a thin layer of glycerine sandwiched between two plexiglass plates, separated

by a gap of width $b \sim 0.5$ mm. Air is injected into the space between the plates via a hole in the centre of the top plate, at a range of pressures between 50 to 150 Torr. The bubble of air does not grow as an expanding circle, but instead undergoes the Mullins–Sekerka instability. In the absence of anisotropy, the instabilities grow in a spatially incoherent way, forming a large-scale structure by the repeated process of tip-splitting, as described above. This structure, which is known as the dense branching morphology, is shown in fig. 2a. It is very clearly not dendritic; indeed, the structure is reminscent of a two-dimensional spherulite.

The growth of the bubble is described by the equation for the evolution of the pressure field, P, in the system. The pressure turns out to be a precise analogue of the concentration field, C, which we have already referred to in section 2. The Navier–Stokes equations, averaged across the gap, show that P obeys the diffusion equation (2.1). The boundary condition at the air–glycerine interface is of the form of the Gibbs–Thomson condition, eq. (2.2), and relates the pressure drop across the interface to the curvature of the interface. (There is a small velocity-dependent modification, due to the presence of a thin wetting layer on the upper and lower plates, which may be neglected for present purposes.)

Fig. 2a is probably the clearest demonstration that diffusion and surface tension are not, on their own, able to account for dendritic growth. Anisotropy was included in the Hele-Shaw cell experiments by engraving a regular grid with four-fold symmetry of depth 0.015 inch on the lower plate. Fig. 2b shows the result: the qualitative features of dendritic growth are reproduced. Further experiments have mapped out a variety of resultant morphologies, as the anisotropy and the pressure are varied [11].

In conclusion, we see that diffusion-controlled growth can, if the effects of crystalline anisotropy are negligible, result in a morphology qualitatively similar to that of spherulites, at least in two dimensions. In the following section, we shall assume that this conclusion is not altered in three dimensions, and that surface tension and diffusion, in the absence of anisotropy, can qualitatively account for the occurence of spherulites.
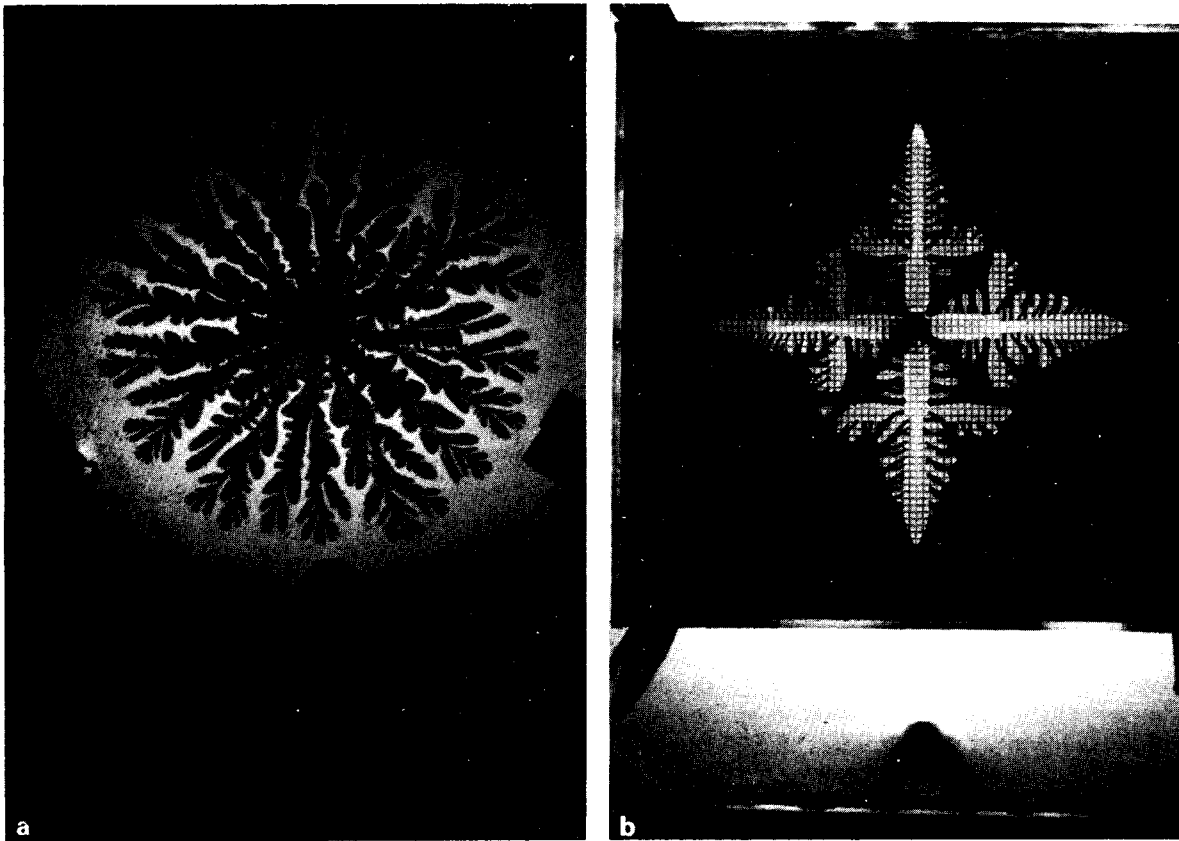
Fig. 2. (a) The dense branching morphology in a 23 inch diameter Hele–Shaw cell, without anisotropy. The structure is created by the growth of a bubble or air growing into a glycerine film sandwiched between the plates. (b) Dendritic growth in a Hele–Shaw cell with anisotropy. The anisotropy was introduced by engraving an grid on the lower plate.

4. Theory of spherulitic growth

In the previous section, I summarized the evidence that crystalline anisotropy plays an important role in diffusion-controlled interface motion, in contrast to the traditional description embodied by eqs. (2.1)–(2.6). This formulation is deficient in another respect, which is crucial for the understanding of spherulitic growth. The Gibbs–Thomson condition, eq. (2.2), is a statement of thermal equilibrium at the interface. During crystal growth, the interface is not static, and this must lead to a departure from the Gibbs–Thomson condition. If the interface is moving at velocity v, then this must be in response to a chemical potential difference, $\Delta\mu$, across the

interface. The most crude approximation – linear response theory – leads to a relation of the form

$$v \simeq \frac{1}{\beta'} \Delta\mu, \qquad (4.1)$$

where β' is a numerical coefficient. $\Delta\mu$ is proportional to the concentration difference between the region ahead of the interface, and the concentration at the interface, i.e. to $\Delta - d_0\kappa - u_s$. Inserting this into eq. (4.1), and rearranging, leads to a modified form of the Gibbs–Thomson condition

$$u_s = \Delta - d_0\kappa - \beta v_n, \qquad (4.2)$$

where β is known as the kinetic coefficient.

This so-called kinetic term is the simplest correction due to non-equilibrium effects. For small

Δ, $v_n \sim \Delta^4$ in the case of dendritic growth [10], and the kinetic term is practically negligible. For larger values of Δ, the diffusion length δ becomes comparable to, or smaller than, the radius of curvature of the solidification front, and the kinetic term is of utmost importance. In particular, the inclusion of the kinetic term can change the character of the dynamics of a planar interface. As noted earlier, except at the special case $\Delta = 1$, eqs. (2.1)–(2.6) do not have a uniformly translating steady state planar interface as a solution. Instead, $v \sim t^{-1/2}$. When the boundary condition, eq. (4.2), is used, however, a uniformly translating planar interface is allowed, provided that $\Delta > 1$. The velocity of the interface is found to be

$$v = (\Delta - 1)/\beta. \tag{4.3}$$

In the case of spherulitic growth, the diffusion length δ is often much smaller than the radius of the spherulite, and so the kinetic term is expected to be important, and $\Delta > 1$. Once the radius of the spherulite is sufficiently large, then locally, the motion is effectively one dimensional, with a uniform velocity in time. Thus, with the inclusion of the kinetic term, $R(t) \sim t$ and $t \to \infty$ rather than the behaviour $R(t) \sim \sqrt{t}$ expected from eqs. (2.1)–(2.6). As the spherulite grows, it should be possible to observe the crossover between the $\sqrt{t}$ and the t behaviour, and indeed, such observations have been reported by Tanaka and Nishi [12] for a system where δ was not much smaller than the spherulite radius.

These considerations lead to the following picture. Keith and Padden have argued convincingly that impurity diffusion is to be expected in spherulite-forming melts. Diffusion-controlled growth can lead, in a natural way, to the spherulitic morphology, firstly because non-equilibrium or kinetic effects can cause the radius of the growing crystal to be linear in time, and secondly because the structure expected for weak or zero anisotropy is characterized by multiple tip-splitting. This accounts for the non-crystallographic branching, a phenomenon inexplicable on the basis of nucleation-controlled growth. Along with Keith and Padden, I presume that microscopic disorder due to kinetic effects is responsible for the low effective anisotropy in these systems; a

more detailed theory of these effects is not possible at present, but the existence of defects in the deposition at the interface is very plausible in light of the chain nature of many spherulite-forming materials.

The major question remaining is how to account for the observed stability of the envelope of the spherulite. The arguments given above deal with spherically symmetrical solutions of the diffusion equation. Linear stability analysis shows that these solutions are unstable, with a stability length as given by eq. (2.9), but with minor modifications due to the kinetic term. Thus, we might heuristically expect that the fibre size is roughly $L_f \sim \lambda_s$, but a convincing analysis beyond linear stability theory is required.

Acknowledgements

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