Pattern formation in solidification

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Regular patterns form in many solidification processes. Examples occur during lamella and rodlike eutectic growth and when single phase cells or dendrites are formed. The scale and regularity of the microstructure determine the properties of the cast materials and is thus important practically. The purpose of the present paper is to show that common features occur in all processes. Steady state analysis indicates that a wide range of possible spacings could occur during eutectic, cellular, or dendritic growth. The degree of freedom is removed by considering the mechanism determining the minimum and maximum spacing on a specimen. It is found that the minimum spacing occurs when the array first becomes stable for a lamella or rodlike eutectic, for cell growth, and for some dendrites. For low temperature gradient, high velocity dendrites the minimum spacing is determined by the spacing when the dendrites first become near enough to interact. The maximum spacing for eutectics and for cells is determined by tip splitting. The maximum spacing for dendrites occurs when a tertiary arm becomes a new primary. Very good agreement is obtained between theory and experiment using this approach to predict spacing limits. The average spacing on a specimen can approach either limit depending on past history. The two extreme spacings are found to span the spacing of the minimum undercooling for eutectic and cellular growth and this allows an average spacing to be estimated using a single condition. It is concluded that three conditions are necessary to form regular structures. A mechanism must exist to eliminate members of the array when the spacing is too small. A mechanism must exist to form new members of the array when the spacing is too wide. The structure must be stable to fluctuations in the range of spacing between the two limits.

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Introduction

Regular patterns form in many solidification processes. Lamella or rodlike structures can be produced in eutectics. Regular cell, or dendrite arrays form during single phase growth. In directionally grown peritectics, the pattern and scale of the microstructure is usually determined by the cells or dendrites of the high temperature phase. In each of these examples the scale of the microstructure can control later reactions and the eventual properties of the material. The purpose of the present paper is to briefly review work on eutectics and to compare it with recent work on cells and dendrites. It will be shown that common features occur in all processes. One of the conclusions reached is that regular structures are not the result of a single growth criterion, but are rather the result of two conditions: one that limits the smallest spacing and one that limits the largest spacing.

Lamella or rodlike eutectics

As the z phase of an A–B eutectic grows B atoms are rejected and at steady state, concentration gradients must build up to transport the B atoms across the lamella to the b phase. The concentration gradient in the liquid near the solid means that if the effect of surface energy is neglected the interface could not be at local equilibrium at more than one point. By adjusting the interface shape a selfconsistent solution can be obtained satisfying curvature undercooling solute and heat flow. Figure 1 shows experimental and calculated interface shapes for a lamella eutectic; note the small radii of curvature near the a/b liquid groove which is needed to compensate for the near eutectic composition in these regions.

A reasonably good solution to the lamella eutectic problem can be obtained without too much difficulty. The earliest models by Zener,1 Tiller,2 or Jackson and Hunt3 produce the correct type of solution at small spacings. The eutectic undercooling is shown to be of the form

$$\Delta T = AVl + (B/l)$$

(1)

1 Calculated and observed interface shapes in carbon tetrabromide–hexachloroethane eutectic×1200

2 Plot of undercooling against spacing: continuous line shows limits of selfconsistent solution; broken line shows equation (1) at large spacings

Figure 1
where $V$ is the velocity, $\lambda$ is the lamella spacing, and $A$ and $B$ are constants. The equation is plotted in Fig. 2 as the continuous line at small spacings then continued as a broken line.

The analytic solution was obtained\(^3\) by approximating the diffusion problem to that of a two phase planar front, and the effect of surface energy was included as an average curvature undercooling. When surface energy is included in this way it appears as if the spacing can be increased at will. At the time of the early work it was pointed out that there was a maximum steady state spacing and an attempt was made to calculate its value. A fully selfconsistent solution shows\(^4\) that as the spacing increases, the tip of the widest phase becomes flat, then a hollow appears, and eventually a steady state solution is not possible.\(^3,4\) The widest growth spacing is probably near the widest steady state spacing. The widest spacing is typically 2–3 times the spacing of the minimum undercooling. Despite this limitation a large range of solutions are possible and these are shown by the continuous line in Fig. 2.

**SPACING SELECTION FOR LAMELLA EUTECTIC**

Experimentally a small range of spacing is found on a specimen. Zener,\(^1\) Tiller,\(^2\) and later workers got rid of the degree of freedom in equation (1) by assuming arbitrarily that growth occurred at the minimum undercooling. This was called the extremum spacing. Although the assumption predicts the experimental average spacing very well there is little justification for its use. By examining the growth process using transparent materials, it was shown\(^3\) that there was a minimum spacing below which one lamella was overgrown by the surrounding lamellae. It was argued\(^3\) that this should occur just before the minimum undercooling. The argument is illustrated in Fig. 3. For a spacing wider than the extremum spacing, a lamella with a slightly narrower spacing will tend to grow at a higher temperature (smaller undercooling). This will mean it will grow ahead and thus grow wider (Fig. 3\(a\)). For a spacing narrower than the extremum spacing, a narrower lamella will grow at a lower temperature, and will grow behind and thus be overgrown (Fig. 3\(b\)). This intuitive approach was justified by later workers.\(^5,6\) The minimum spacing is the smallest spacing which is stable to perturbations in spacing. This is referred to below as the array stability limit. It is concluded that lamella eutectic structures grow somewhere between minimum and maximum spacing. For a lamella eutectic, the assumption that growth occurs at the minimum undercooling is reasonably valid because it predicts a spacing somewhere between the minimum and maximum

1: initial interface position; 2: formation of narrower lamellae; 3: change in interface shape owing to change in local undercooling

**Growth of lamellae that are a wider and b narrower than extremum spacing:** condition \(a\) leads to restabilisation of array; \(b\) leads to overgrowth

**Transverse section of Al–0.5Mn alloy grown at 1 mm s\(^{-1}\)**

**Plot of dimensionless undercooling $\Delta T^*$, velocity $V^*$, and spacing $\lambda^*$:** dimensionless terms are defined in Ref. 8

**Calculated interface shapes for a cells and b dendrites**
Constant velocity section from Fig. 5, showing cell and dendrite regions and stable bands

Possible spacings. Although the discussion has considered lamella growth, similar considerations apply to rodlike eutectic growth.

**Single phase growth**

When growth occurs in a positive temperature gradient, a planar interface is stable at a low enough and high enough velocity. Between these velocities arrays of cells or dendrites can be formed. An example of a cell structure is shown in Fig. 4. As the cell or dendrite grows solute is rejected in front and to the sides of the tip. Depending on the spacing and tip radius, the diffusion fields overlap and an interaction occurs between neighbours. To model cellular growth, a smooth steady state interface shape is needed which satisfies curvature undercooling, solute, and heat flow at all points on the interface. Numerical solutions have been obtained for smooth axisymmetric shapes. The axisymmetric cylinder is intended to approximate to one member of a hexagonal array. An example of the calculated results for a fixed temperature gradient is shown in Fig. 5, which is a plot of undercooling against spacing and velocity. The smallest velocity shown is approximately the constitutional undercooling velocity and the largest the absolute stability limit; outside these limits growth should occur with a planar front.

A feature of the numerical work was that smooth cell and dendrite-like shapes were found on different regions of Fig. 5. It will be shown below that, despite the fact that the dendrite arms are not modelled, the predictions using the smooth dendrite shapes agree very well with experiment. The smooth dendrite shapes are taken to be a representation of the averaged fraction solid. This in fact was the assumption made in all analytic models of dendritic growth. Traditionally cells are considered to be dendrites without arms. A conclusions from the numerical work is that a better way to differentiate them is to consider the interface shape. For a dendrite, the interface near the tip is a paraboloid of revolution and the tip has the smallest radius of curvature (Fig. 6b). For a cell, the interface is almost spherical but tends to have the largest radius of curvature at the tip (Fig. 6a).

At a constant velocity, cells occur at small spacings and dendrites at large spacings. A plot of undercooling against spacing for a particular velocity is shown in Fig. 7. There are separate lines for cells and dendrites and these appear as different surfaces in Fig. 5.

As for the lamella eutectic, there is a maximum spacing for cells; as this spacing is approached the cell becomes flat at the tip and eventually a steady state solution can not be obtained. There appears to be no maximum spacing for dendrites.

**SPACING SELECTION FOR CELLS AND DENDRITES**

From Fig. 7 it is apparent that a condition is necessary to fix the spacing or conditions are necessary to fix a range of spacing. Experimental studies of the space change mechanisms have been carried out over many years. These are illustrated schematically in Fig. 8. When the spacing is too wide, a hollow appears in the centre of a cell and the tip splits giving an additional member of the array. For dendrites a different process occurs. When the spacing is too wide, a tertiary arm catches up the front and becomes a new primary arm. When the spacing is too narrow, a slightly smaller member of the array gets smaller and becomes overgrown by its neighbours (Fig. 8).

The maximum spacing for cells can be treated by examining the time dependent growth of a single cell. It was found that the maximum stable spacing for cells was close to the maximum steady state spacing. The maximum spacing for dendrites can not be modelled by the smooth interface model under discussion. It would be expected to depend on the competitive growth between the tertiary and the next secondary arm. It is clear that the maximum spacing must be greater than twice the minimum spacing otherwise the new dendrite can not catch up. In this discussion the maximum dendrite spacing is taken to be twice the minimum spacing.

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**Overgrowth**

![Overgrowth](image1)

**Stable**

![Stable](image2)

**Tip splitting**

![Tip splitting](image3)

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**Overgrowth**

![Overgrowth](image4)

**Stable**

![Stable](image5)

**Growth of tertiary arm**

![Growth of tertiary arm](image6)

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8 Schematic representation of spacing adjustment mechanism for cells and dendrites
When the spacing is too narrow overgrowth occurs until one of two things happens:

(i) the array becomes stable: any small local variation in spacing tends to be reversed and the spacing of the array becomes more uniform. The spacing when this first takes place has been termed the array stability limit. It is felt that the presence of a stable array is an essential feature of the formation of regular structures. Both cells and dendrites can interact in this manner

(ii) as the spacing is increased the array does not become stable but instead the dendrites eventually become so far apart that they no longer interact with one another. The spacing when interaction first becomes appreciable has been termed the interaction limit; the amount of overlap is defined in Ref. 9.

If an array stability limit exists it must occur at a smaller spacing than the interaction limit since interaction is necessary for a stable array.

In earlier work a multicell–dendrite model was used to examine stability. The model was set up with a slightly smaller central cell surrounded by six others. The problem was started by using compositions obtained for steady state single cells. It was found that when the wall composition near the tip was initially such that solute flowed from a wider to a narrower cell the narrower cell was slowed down and was overgrown (Fig. 9a). Conversely, when solute initially flows from the narrower to the wider dendrite the narrower cell grew more easily and a stable array was formed (Fig. 9b). This is an intuitively reasonable condition and might have been anticipated. The condition was applied to the simpler single cell model to predict the array stability limit.

A search is made for the spacing when the wall composition adjacent to the tip of a narrower dendrite first becomes larger than that of a slightly wider dendrite. The search is illustrated in Fig. 10, which shows calculated dendrite wall compositions plotted against distance for five spacings. The position of the tip is shown by a square for each spacing. The spacing increases in the order 1–5 and for dendrites the tip undercooling decreases with increasing spacing so that the tip position moves from left to right of Fig. 10 as the spacing increases. Considering the wall composition near the tips for dendrites 1 and 2, the line for the wider spaced dendrite 2 is above that for 1 and thus the array is unstable (Fig. 9a). On the other hand, for dendrites 4 and 5 the wall composition for the wider spacing dendrite 5 is lower than that for spacing 4 and thus the array is stable (Fig. 9b). The transition occurs somewhere between spacing 2 and spacing 3.

The transition was searched for numerically and typical results together with maximum spacing predictions are shown in Figs. 5 and 7.

For high velocities and low temperature gradients it was found that the dendrite array did not become stable before the interaction limit. An example of the calculated minimum spacing as a function of velocity is shown in Fig. 11. At low velocities the minimum spacing is determined by the array stability limit (line a) and at high velocities by the interaction limit (line b). Interaction of the diffusion fields occurs for any spacing below the interaction limit line. The interaction leads to a loss of a dendrite unless the array is stable. There are three regions and these are shown in Fig. 11: region A where the dendrites are so far apart that no interaction takes place and irregular structures are formed; region B where overgrowth occurs leading to an increase in the average spacing; region C where the array is stable and regular structures can be formed.

**COMPARISON WITH EXPERIMENT**

Correlation of experiment with theory is shown in Figs. 12–14, for cells and dendrites. Figure 12a shows a comparison of the predicted stable band with the results from Eshelman et al. for succinonitrile–acetone and Fig. 12b shows a comparison with the balanced pseudo-binary system of Al–Si–Mg. Figure 12c shows the array stability limit for dendrites (continuous line) compared with the results of Somboonsuk et al. The average spacing is expected to be greater than the array stability limit. Correlation with gradient is shown by the continuous lines in Fig. 12d and with composition in Fig. 12e.

Huang et al. investigated dendrite spacing limits experimentally by using stepped increments or decrements in velocity. The work is shown in Fig. 13. Overgrowth occurred for the spacings shown by the open circles. This should be compared with the array stability limit (lower line). Tertiary arms grew between dendrites for the
open triangles. This appears to be larger than the factor of two times the array stability limit suggested by earlier work.

The minimum dendrite spacings for all cases in Figs. 12 and 13 were determined by the array stability limit. A correlation of the predicted minimum spacing, where the spacing is determined by the array stability limit at low velocities and the interaction limit at high velocities, is shown in Fig. 14. The agreement is good both for the transition velocity and for the different dependence of spacing on velocity. As expected, for velocities below the transition velocity the spacings were relatively uniform but for higher velocities the spacing was almost random. The high velocity effect can be equally well regarded as a low gradient effect. This is the reason why a regular spacing is not generally found in castings.

The numerical results have been fitted by approximate analytical expressions. These may be used to compare experiment with theory without carrying out numerical calculations. The expressions are given in the Appendix and are shown in Fig. 12 as broken lines.

Discussion and conclusions

The factors controlling lamella eutectic, cell, and dendritic growth are very similar. To predict spacing it is necessary to consider and model the mechanisms that limit the minimum and maximum spacing. Between the two limits the regularity of the structure depends on whether the array is stable. For a stable array any local variation in spacing tends to decay, leading to a more uniform spacing.

The maximum spacing occurs when a mechanism leads to the formation of a new member of the array. For a lamella eutectic and for cells the interface for a single member of the array becomes unstable and the tip splits. For dendrites a tertiary arm moves forward and becomes a new primary. This occurs when a tertiary arm competes successfully with the next secondary arm. For lamella eutectics, cells, and some dendrites the minimum spacing is determined by the spacing when the array first becomes stable. When this occurs regular structures are formed. For

Comparison of theory and experiment:

experiments were performed with stepped increments or decrements in velocity; solid and open circles might be expected to agree with array stability limit (lower line)
dendrites grown at low gradients and high velocity, the array does not become stable and dendrites are lost until
the tips are far enough apart for no interaction. Any spacing up to the maximum can then exist on the specimen.

The average spacing on a specimen has little real
meaning. If the growth velocity is slowly decreasing the
average spacing is found to migrate towards the minimum
spacing. If the growth rate is gradually increasing the
average spacing is found to migrate towards the minimum
spacing. If the growth velocity is slowly decreasing the
average spacing is found to migrate towards the minimum
spacing. If the growth velocity is slowly decreasing the
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spacing. If the growth velocity is slowly decreasing the
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spacing.

The predicted undercooling and minimum spacing
obtained using the numerical model9,10 have been fitted
using analytical expressions9,17. These expressions allow
experimental results to be compared with theory without
using the numerical model.

An expression was given for dendrites in Ref. 9, but a
better expression was obtained in Ref. 17: the latter behaves
more realistically as k → 0. The dimensionless dendrite
undercooling can be represented by

\[ \Delta T^* = \frac{G^*}{V^* \Gamma} + \frac{k h(p)}{1 - I(p)(1 - k)} + 0.33(0.1 \Delta T^* - G^* \delta) \]

where

\[ \rho = V^{0.5}(1 - G^*/V^*) \]

and

\[ I(p) = p \exp(p) E_1(p) \]

is the Ivantsov function,18 and can be evaluated using
rational or polynomial expansions.19

The minimum primary spacing or array stability limit is
given by the smaller of

\[ \lambda^* = 2.5 \sqrt{V^*} \left[ 1 - (G^*/V^*) \right]^{0.5} G^* - 2(1 - \delta)^{3/2} \]

\[ \lambda^* = 12 V^* - 1 \]

where \( \delta = 0.3 + 1.9G^* \). It was found that the results for
cells could be fitted6 by

\[ \Delta T^* = \frac{G^*}{V^* \Gamma} + a + (1 - a) V^{0.45} \frac{G^*}{V^*} \left[ 1 - (1 - a) V^{0.45} \right] + b(V^* - G^* \delta) \left[ 1 - V^* \right]^{0.5} \]

where

\[ a = 5.273E - 3 + 0.5519k - 0.1865k^2 \]

\[ b = 0.5882 - 0.2267 \log k + 0.2034(\log k)^2 \]

The numerical results for spacing may be fitted by an
expression of the form

\[ \lambda^* = \lambda_0^* \left[ 1 - \frac{1}{a(V^*)} \right] \mid \lambda_0^* \]

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