CHAPTER 8

DENDRITIC GROWTH

Movies from experiments and simulations of dendritic growth can be found at: http://solidification.org/Movies/dendritic.html

8.1 INTRODUCTION

The preceding chapter focused on nucleation, i.e., the first appearance of solid in the melt, and in this context the nucleus was treated as a sphere or a spherical cap. As the solid grows, the spherical morphology eventually becomes unstable, which leads to the formation of dendrites. This is the topic of the present chapter. Figure 8.1 shows several examples that are discussed further in Sect. 8.2.

We divide the subject into a discussion of free growth, the evolution of one isolated solid particle in an infinite undercooled melt, and a discussion of constrained growth, where many solid structures grow in concert under an imposed thermal gradient. The important physical phenomena are described, with a particular focus on the development of microstructural length scales by the interaction between capillarity and transport of heat and solute. We begin each section with general observations regarding microstructural features, and how their formation is related to processing conditions. For certain simple shapes, these qualitative descriptions are augmented by a formal stability analysis of the base growth morphology, a sphere for free growth and a planar front for constrained growth. These analyses help us derive expressions relating the processing conditions to material properties and microstructure. Such models can be used to predict microstructures in more complex geometries and processing conditions, as is demonstrated in subsequent chapters. We also discuss the effect of melt convection on the final microstructure.
Dendritic growth

Fig. 8.1 (a) A micrograph of a pure succinonitrile dendrite solidifying in an undercooled melt with $\Delta T = 0.8$ K. (Reproduced with permission from C. Beckermann) (b) A spot-weld in a Ni-based superalloy. (Reproduced with permission from ref. [12]) (c) A photograph of a Bi crystal grown from a chill inserted into an undercooled melt. (d) A micrograph of a quenched interface in a directionally solidified Si-Al alloy, displaying faceted Si primary dendrites (Reproduced with permission from ref. [44]).

8.2 FREE GROWTH

8.2.1 General observations

Let us begin the discussion where we left off in the previous chapter, i.e., with a spherical solid nucleus of radius greater than the critical radius, $R_c = 2 \Gamma_{st}/\Delta T$, growing in a pure, infinite and undercooled melt. The temperature at infinite distance from the nucleus is $T_\infty = T_f - \Delta T$, where $\Delta T$ is the undercooling. We refer to this configuration as free growth. It was demonstrated in Chap. 7 that it is energetically favorable for the sphere to continue to grow as soon as $R > R_c$. One might then expect that under these conditions, the sphere would continue to grow until reaching macroscopic dimensions. Indeed, in Sect. 5.4.1, we computed the temperature profiles in the solid and liquid assuming this to be the case. However, as the sphere grows, the spherical morphology becomes unstable with respect
to perturbations in shape. A formal stability analysis is given later to help understand the details of the emergence of the microstructure pattern during growth.

Once disturbances to the spherical shape can grow, i.e., after the spherical morphology is unstable, the solid shape begins to express the preferred growth directions of the underlying crystal. This preference is derived from anisotropy; whether it be in the surface energy of the solid-liquid interface, in the ease of attachment of atoms to the interface on different crystallographic planes, or both. These phenomena were first introduced in Chap. 2. The fully developed structure looks quite different from the initial sphere. Figure 8.1(a) shows a crystal of succinonitrile (SCN) growing in an undercooled melt. This material, which crystallizes with a BCC structure, has been used extensively in solidification studies due to the fact that it behaves similarly to metals, as well as it being transparent. The solid takes on a tree-like form, called a dendrite, consisting of a primary trunk growing along one of the six equivalent \( \langle 100 \rangle \) directions of the crystal, with secondary arms in the four conjugate \( \langle 100 \rangle \) directions appearing just behind the advancing dendrite tip. The \( \langle 100 \rangle \) preferred growth direction is typical of BCC crystals, and reflects the underlying surface energy anisotropy, even though the anisotropy represents only a few percent of the actual value of the surface energy. Preferred growth directions for other crystal structures are tabulated in Table 8.1. Figure 8.1(b) shows a regular array of Ni-rich dendrites formed during solidification of a superalloy weldment. This configuration is referred to as constrained growth, and is discussed in detail in Sect. 8.3.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Preferred growth direction</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCC</td>
<td>( \langle 100 \rangle )</td>
<td>Al, Cu, Ni, ( \gamma )-Fe</td>
</tr>
<tr>
<td>BCC</td>
<td>( \langle 100 \rangle )</td>
<td>( \delta )-Fe, Succinonitrile (SCN), ( \text{NH}_4\text{Cl} ) (CsCl-type)</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>( \langle 110 \rangle )</td>
<td>Sn</td>
</tr>
<tr>
<td>HCP</td>
<td>( \langle 10\overline{1}0 \rangle )</td>
<td>Zn, ( \text{H}_2\text{O} )</td>
</tr>
</tbody>
</table>

In most metallic systems, where interface attachment kinetics is negligible, the preferred crystallographic growth directions are a consequence of the anisotropy of the solid-liquid interfacial energy. In general, as the anisotropy of \( \gamma_{sl} \) increases, assuming that all other quantities remain the same, the dendrite will exhibit a sharper and sharper tip. If the anisotropy in \( \gamma_{sl} \) is sufficiently large, the dendrites will present a faceted morphology. As two examples of this morphology, Fig. 8.1(c) shows a crystal of pure Bi grown from an undercooled melt, and Fig. 8.1(d) displays an array of faceted Si dendrites growing during directional solidification in a Si-Al alloy. In the Bi crystal, one can clearly see facets of the rhombohedral crystal growing in a spiral pattern, probably originating from a screw dislocation.
on the initial surface. In such materials, the kinetics of atom attachment at the interface also plays a significant role.

Let us consider further dendrites in metals, for which the anisotropy in $\gamma_{st}$ controls the growth direction, at least at low undercooling. It is difficult to measure the surface energy itself accurately, and even more so for its anisotropy. It has been observed that materials with high values of surface energy anisotropy, typically ionic crystals such as oxides, fluorides or ice, also tend to have relatively large entropies of fusion. Indeed such systems exhibit a large difference in organization between the liquid and solid phases, i.e., a large entropy of fusion. This led Jackson [24] to define a rule of thumb that faceted crystals form in materials for which $\Delta S^m_f/R > 2$, where $\Delta S^m_f = M L_f / T_f$ is the molar entropy of fusion and $R$ is the ideal gas constant (see Chap. 2). Table 8.2 gives examples of entropies of fusion for several common materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$L_f$ (J g$^{-1}$)</th>
<th>$M$ (g mol$^{-1}$)</th>
<th>$T_f$ (K)</th>
<th>$\Delta S^m_f/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Non-faceting materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>373</td>
<td>26.982</td>
<td>933</td>
<td>1.30</td>
</tr>
<tr>
<td>Cu</td>
<td>211</td>
<td>63.546</td>
<td>1356</td>
<td>1.19</td>
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<tr>
<td>Ni</td>
<td>298</td>
<td>58.693</td>
<td>1728</td>
<td>1.22</td>
</tr>
<tr>
<td>Sn</td>
<td>59.2</td>
<td>118.71</td>
<td>504</td>
<td>1.68</td>
</tr>
<tr>
<td>SCN</td>
<td>43.8</td>
<td>80.1</td>
<td>331</td>
<td>1.27</td>
</tr>
<tr>
<td>Zn</td>
<td>112</td>
<td>65.409</td>
<td>693</td>
<td>1.27</td>
</tr>
<tr>
<td><strong>Faceting materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>54</td>
<td>208.98</td>
<td>544</td>
<td>2.50</td>
</tr>
<tr>
<td>Si</td>
<td>1790</td>
<td>28.086</td>
<td>1687</td>
<td>3.59</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>334</td>
<td>18</td>
<td>273</td>
<td>2.65</td>
</tr>
</tbody>
</table>

8.2.2 Surface energy anisotropy, stiffness and equilibrium shape

Since the surface energy and its anisotropy play such important roles in dendritic growth, it is worth discussing these properties in greater detail. The topic was introduced in Sect. 2.4.2, and we first recall certain points from that discussion for the current context. In 2-D, one often represents the surface energy in the form

$$\gamma_{st} = \gamma_{st}^0 [1 + \varepsilon_n \cos(n\phi)]$$

(8.1)

where $\phi$ is the azimuthal angle measured from a reference direction, $\varepsilon_n$ represents the strength of the anisotropy and $n$ is the degree of symmetry. For example, $n = 4$ for cubic symmetry in a (100) plane, and $n = 6$ for hexagonal symmetry in a (0001) plane. The surface stiffness $\Psi_{st}$, defined
in Eq. (2.65), is given in 2-D by

$$\Psi_{s\ell} = \gamma_{s\ell} + \frac{d^2\gamma_{s\ell}}{d\phi^2}$$  \hspace{1cm} (8.2)

Thus, for a fourfold symmetry in 2-D, we have

$$\Psi_{s\ell} = \gamma_{s\ell}^0 [1 - 15\varepsilon_4 \cos(4\phi)]$$  \hspace{1cm} (8.3)

Notice that, if $\varepsilon_4 > 1/15$, there are some angles $\phi$ for which the surface stiffness becomes negative. This is forbidden by thermodynamics, and results in a range of orientations of the surface normal with respect to the crystal axis that cannot appear. The equilibrium shape of the crystal, computed using the Wulff construction (see Sect. 2.4.2), is illustrated in Fig. 8.2 for two values of $\varepsilon_4$, one above and the other below this transition. The “ears” along the axes at the cusp of the Wulff shape for $\varepsilon_4 = 0.15$, drawn in red, correspond to the orientations that are missing in the equilibrium crystal shape.

![Wulff shape and missing orientations](image.png)

**Fig. 8.2** The equilibrium shape of fourfold symmetric 2-D crystals. (a) $\varepsilon_4 = 0.05$. The Wulff shape has been drawn inside of $\gamma_{s\ell}$ for clarity. (b) $\varepsilon_4 = 0.15$. Notice the “ears” on the coordinate axes, corresponding to the missing orientations.

We will see later in this chapter that the surface energy anisotropy plays a key role in determining the preferred growth direction for dendrites. There are two common “rules of thumb” for the selection of the preferred growth direction:

1. **Maximum surface energy**: The basis for this conjecture is that the crystal will seek to minimize its total surface energy, which it can accomplish by creating relatively higher curvature in the direction corresponding to maximum surface energy.
2. Minimum surface stiffness: The crystal will prefer to grow in the direction where the surface presents the smallest resistance to being deformed.

For the anisotropy relation we just examined, these two rules of thumb provide the same result, namely that the dendrites should prefer to grow in \( \langle 10 \rangle \) directions. We will see later, in Sect. 8.3, that the minimum surface stiffness rule is closer to what is observed experimentally.

These concepts can be extended to 3-D, but one must be somewhat more formal. The stiffness, which was a scalar in 2-D, becomes a tensor in 3-D:

\[
\Psi_{ij} = \gamma_{s\ell} \delta_{ij} + \frac{\partial^2 \gamma_{s\ell}}{\partial \zeta_i \partial \zeta_j}
\]

(8.4)

where \( \delta_{ij} \) is the Kronecker delta, and \( \zeta_1 \) and \( \zeta_2 \) define coordinates along orthogonal directions on the surface perpendicular to the normal vector \( n \). Any material property must be independent of the coordinate system used to describe it, and so we need only the trace of \( \Psi \), which is invariant under rotation about \( n \). Choosing the spherical coordinate system, where the polar angle \( \theta \) is measured from the \([001]\) direction, and the azimuthal angle \( \phi \) is measured as in 2-D, from the \([100]\) direction in the \((001)\) plane, we have

\[
\text{tr}(\Psi_{s\ell}) = 2\gamma_{s\ell} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial \gamma_{s\ell}}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \gamma_{s\ell}}{\partial \phi^2}
\]

(8.5)

For crystals with a cubic symmetry, the surface energy can be expanded in terms of cubic harmonics, i.e., orthogonal combinations of spherical harmonics that have cubic symmetry:

\[
\gamma_{s\ell}(n) = \gamma_{s\ell}^0 (1 + a_1 [Q_4 - 3/5] + a_2 [3Q_4 + 66S_4 - 17/7] + \ldots)
\]

(8.6)

where \( a_1 \) and \( a_2 \) parameterize the strength of the anisotropy. The functions \( Q_4 \) and \( S_4 \) are written in Cartesian and spherical forms as

\[
Q_4 = \begin{cases} 
{n_x^4 + n_y^4 + n_z^4} \\
\sin^4 \theta \left( \cos^4 \phi + \sin^4 \phi \right) + \cos^4 \theta
\end{cases}
\]

(8.7)

\[
S_4 = \begin{cases} 
{n_x^2 n_y^2 n_z^2} \\
\sin^4 \theta \cos^2 \theta \sin^2 \phi \cos^2 \phi
\end{cases}
\]

(8.8)

The Cartesian components of the unit normal \( n \) in this reference frame correspond to \( n_x, n_y \) and \( n_z \). We further note that it is possible to choose \( a_1 \) and \( a_2 \) such that the expression in Eq. (8.6) becomes equivalent to Eq. (8.1) in the \((001)\) plane (see Exercise 8.2). The Wulff shape can be computed, using the formalism of Cahn and Hoffman [10], as the surface swept by the vector \( \xi \), defined as

\[
\xi = \nabla[r \gamma_{s\ell}(\hat{n})] = \gamma_{s\ell} \hat{n} + \frac{\partial \gamma_{s\ell}}{\partial \theta} \hat{\theta} + \frac{1}{\sin \theta} \frac{\partial \gamma_{s\ell}}{\partial \phi} \hat{\phi}
\]

(8.9)
where \( r = (x^2 + y^2 + z^2)^{1/2} \). The \( \xi \)-vector can be used to compute the surface tension vector, \( \sigma_{s\ell} = \xi \times t \) in the direction of any unit vector \( t \) in the solid-liquid interface. In the literature, surface energy (a scalar) and surface tension (a vector) are often confused because they have equivalent units (Jm\(^{-2} \), Nm\(^{-1} \)). However, the equivalence between the two quantities is valid only when \( \gamma_{s\ell} \) is isotropic, in which case \( \sigma_{s\ell} \) is always parallel to \( t \), and thus has the same magnitude as \( \gamma_{s\ell} \).

Examples of the shape of \( \gamma_{s\ell} \) for various values of the parameters, equivalent in the (001) plane to those in Fig. 8.2, are given in Fig. 8.3, along with their corresponding Wulff shapes. The “ears” that were present in 2-D, and which become “flaps” along some edges in 3-D, again indicate a band of forbidden orientations. They have been removed in Fig. 8.3(d) for the sake of clarity. One can see that the behavior in 3-D is considerably more complicated in comparison to 2-D.

![Fig. 8.3](image)

(a) \( \gamma_{s\ell}, a_1 = 0.0568, a_2 = 0.0477 \)  
(b) \( \gamma_{s\ell}, a_1 = 0.1705, a_2 = 0.1432 \)  
(c) \( \xi, a_1 = 0.0568, a_2 = 0.0477 \)  
(d) \( \xi, a_1 = 0.1705, a_2 = 0.1432 \)

**Fig. 8.3** (a)-(b) The surface energy \( \gamma_{s\ell} \) of 3-D crystals with levels of cubic anisotropy comparable with those in Fig. 8.2. (c)–(d) The corresponding \( \xi \)-vector surfaces, equivalent to equilibrium shape crystals. The “ears” and “flaps” corresponding to missing orientations have been removed in (d).