1
Introduction

1.1
The Role of Microstructure Materials Science

The properties of most engineered materials have a connection with their underlying microstructure. For example, the crystal structure and impurity content of silicon will determine its band structure and its subsequent quality of performance in modern electronics. Most large-scale civil engineering applications demand high-strength steels containing a mix of refined crystal grains and a dispersion of hard and soft phases throughout their microstructure. For aerospace and automotive applications, where weight to strength ratios are a paramount issue, lighter alloys are strengthened by precipitating second-phase particles within the original grain structure. The combination of grain boundaries, precipitated particles, and the combination of soft and hard regions allow metals to be very hard and still have room for ductile deformation. It is notable that the lengthening of span bridges in the world can be directly linked to the development of pearlitic steels. In general, the technological advance of societies has often been linked to their ability to exploit and engineer new materials and their properties.

In most of the above examples, as well as a plethora of untold others, microstructures are developed during the process of solidification, solid-state precipitation, and thermomechanical processing. All these processes are governed by the fundamental physics of free boundary dynamics and nonequilibrium phase transformation kinetics. For example, in solidification and recrystallization – both of which serve as a paradigm of a first-order transformation – nucleation of crystal grains is followed by a competitive growth of these grains under the drive to reduce the overall free energy – bulk and surface – of the system, limited, however, in their kinetics by the diffusion of heat and mass. Thermodynamic driving forces can vary. For example, solidification is driven by bulk free energy minimization, surface energy and anisotropy. On the other hand, strain-induced transformation must also incorporate elastic effects. These can have profound effects on the morphologies and distribution of, for example, second-phase precipitates during heat treatment of an alloy.

The ability to model and predict materials' properties and microstructures has greatly benefited from the recent "explosion" of new theoretical and numerical tools. Modern parallel computing now allows billions of atoms to be simulated for times on the scale of nanoseconds. On higher scales, various continuum and sharp interface methods have made it possible to quantitatively model free surface kinetics responsible for microstructure formation. Each of these methodologies, however, comes with its advantages and deficiencies.

1.2
Free Boundary Problems and Microstructure Evolution

Solidification has typically served as a paradigm for many classes of nonequilibrium phase transformations that govern the formation of complex microstructure during materials processing. The most commonly recognized solidification microstructure is the tree-like *dendrite* pattern (which comes from the Greek word for tree, "dendron"). The most popular example of a dendrite is a snowflake, which is a single crystal of ice, solidified from water that falls through the sky. Figure 1.1 shows an image of a branch of a snowflake in an organic material known as succinonitrile (SCN) solidifying from its melt. This material is a favorite with researchers because it solidifies at room temperature and is transparent, affording us a good look at the solidification process. It is also often referred to as a "metal analogue" as it solidifies into a cubic crystal structure. Surprisingly, the properties learned from this organic material essentially remain unchanged qualitatively in metals and their alloys. Patterns like the one in Figure 1.1 are not limited to solidification. They are also found in solid-state transformations. Figure 1.2 shows dendrite patterns that emerge when one solid phase emerges from and grows within another. Microstructure modeling involves understanding the physics governing such microstructure formation.


Figure 1.1 A snowflake of succinonitrile, an organic compound that solidified at room temperature. The image shows the characteristic "dendritic" tree-like pattern of the crystal, typical of crystal formation in nearly all anisotropic solids. It is a ubiquitous shape that depends on the physics of reaction–diffusion and the properties of the surface energy between the solid and the liquid. Vincent Proton, McMaster University, 2008.
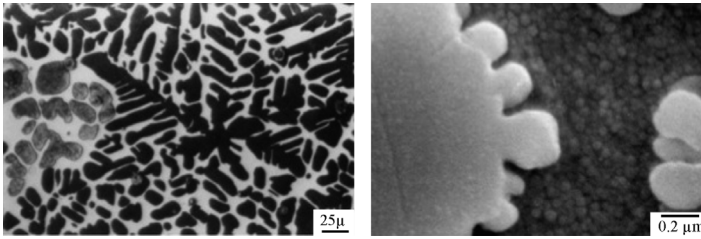
Figure 1.2 *Left*: Solid-state dendrites in an alloy of copper (Cu) and zinc (Zn). *Right*: Dendrite in a nickel-based superalloy, a material commonly used in aerospace because of its very high strength. Reprinted from Refs [1] (left) and [2] (right).

Solidification is at the heart of all metal casting technologies. Figure 1.3 shows a typical layout for casting slabs of steel used in many industries. The basic idea is that a liquid metal alloy enters a region like the one between the rollers in the figure. There the liquid is sprayed with water, which establishes a cooling mechanism that extracts heat from the casting at some rate ($\dot{Q}$). The liquid solidifies from the outer surface inward. The rate at which heat is extracted – that is, the cooling rate – is key to establishing the morphology and scale of the solidification microstructure, as seen in the inset of Figure 1.3. Typical dendrite microstructures in many steel alloys resemble those shown in Figure 1.4. In this situation, the competitive growth and interaction of
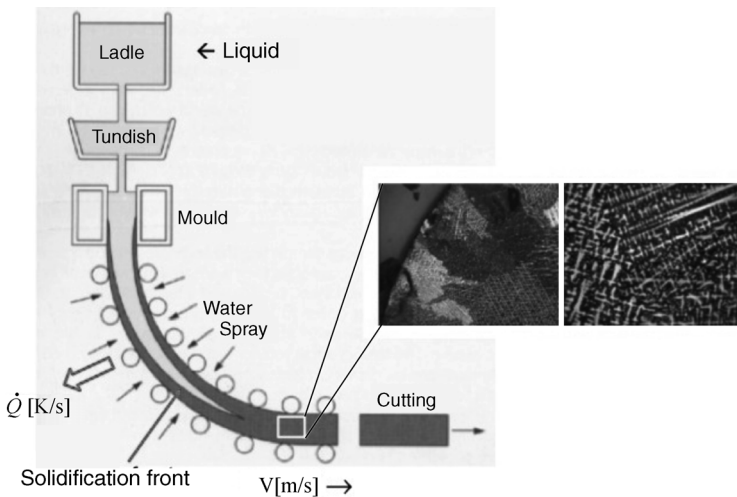
Figure 1.3 Typical industrial layout for thin slab casting. Liquid is entered from top, is cooled by splashing water, and is directed – as it solidifies – at some speed (V) to the right. Most steels will then be cut and thermomechanically treated to improve their strength properties. In spite of the postsolidification treatment that the metal may receive, the so-called "as-cast" structure (inset) that is established initially is always, to some extent, present in the final product.

Dendrites

Increasing cooling rate
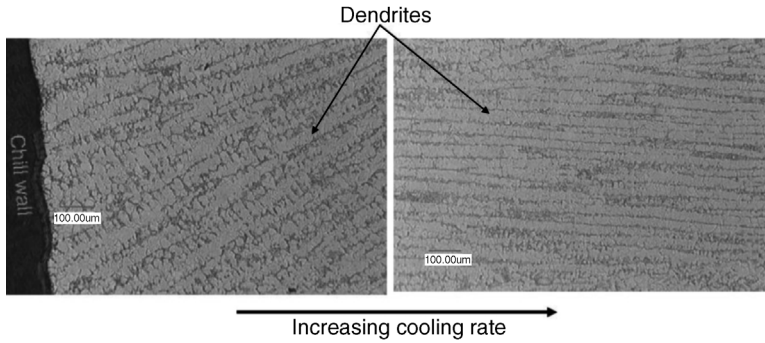
Figure 1.4 Dendrite arrays in a steel alloy. Growth is from bottom left to top right in the left figure and from left to right in the right figure. The figure on the right has been cooled much more rapidly than that on the left. The main striations are known as primary dendrites. The budding branch-like structures coming off the primary dendrites are known as secondary arms or side branches.

a very large number of dendrites means that only partial traces of the traditional snowflake pattern survive. In fact, depending on the direction of heat extraction, cooling rate, and geometry of the cast, it is typical that only single "arms" of the characteristic snowflake pattern survive and grow. These form the branch-like striations in the figure.

The kinetics of microstructure formation is traditionally modeled by a set of mathematical relations that describe the release and diffusion of heat, the transport of impurities, and the complex boundary conditions that govern the thermodynamics at the interface. These mathematical relations in theory contain the physics that gives rise to the complex structure shown in the above figures. As a concrete example, in the solidification of a pure material the advance of the solidification front is limited by the diffusion of latent heat away from the solid–liquid interface, and the ability of the interface to maintain two specific boundary conditions; flux of heat toward one side of the interface is balanced by an equivalent flux away from the other side, and the temperature at the interface undergoes a curvature correction known as the Gibbs–Thomson condition. These conditions are mathematically expressed in the following *sharp interface model*, commonly known as the Stefan problem:

$$
\begin{aligned}
\frac{\partial T}{\partial t} &= \nabla \cdot \left(\frac{k}{\varrho c_p} \nabla T \right) \equiv \nabla \cdot (\alpha \nabla T) \\
\varrho L_f V_n &= k_s \nabla T \cdot \vec{n}\big|_{\text{int}}^{s} - k_L \nabla T \cdot \vec{n}\big|_{\text{int}}^{L} \\
T_{\text{int}} &= T_m - \left(\frac{\gamma T_M}{L_f} \right) \kappa - \frac{V_n}{\mu}
\end{aligned}
\tag{1.1}
$$

where $T \equiv T(\vec{x}, t)$ denotes temperature, k thermal conductivity (which assumes values k_s and k_L in the solid and liquid, respectively), ϱ the density of the solid and

liquid, c_p the specific heat at constant pressure, α the thermal diffusion coefficient, L_f the latent heat of fusion for solidification, γ the solid–liquid surface energy, T_M the melting temperature, κ the local solid–liquid interface curvature, V_n the local normal velocity of the interface, and μ the local atomic interface mobility. Finally, the subscript "int" refers to interface and the superscripts "s" and "L" refer to evaluation at the interface on the solid and liquid side, respectively.

Like solidification, there are other diffusion-limited phase transformations whose interface properties can, on large enough length scales, be described by specific sharp interface kinetics. Most of them can be described by sharp interface equations analogous to those in Equation 1.1. Such models – often referred to as sharp interface models – operate on scales much larger than the solid–liquid interface width, itself of atomic dimensions. As a result, they incorporate all information from the atomic scale through effective constants such as the capillary length, which depend on surface energy, the kinetic attachment coefficient, and thermal impurity diffusion coefficient.

1.3
Continuum versus Sharp Interface Descriptions

A limitation encountered in modeling free boundary problems is that the appropriate sharp interface model is often not known for many classes of phenomena. For example, the sharp interface model for phase separation or particle coarsening, while easy to formulate nominally, is unknown for the case when mobile dislocations and their effect of domain coarsening are included [3]. A similar situation is encountered in the description of rapid solidification when solute trapping and drag are relevant. There are several sharp interface descriptions of this phenomenon, each differing in the way they treat the phenomenological drag parameters and trapping coefficients and lateral diffusion along the interface.

Another drawback associated with sharp interface models is that their numerical simulation also turns out to be extremely difficult. The most challenging aspect is the complex interactions between topologically complex interfaces that undergo merging and pinch-off during the course of a phase transformation. Such situations are often addressed by applying somewhat arbitrary criteria for describing when interface merging or pinch-off occurs and by manually adjusting the interface topology. It is worth noting that numerical codes for sharp interface models are very lengthy and complex, particularly in 3D.

A relatively new modeling paradigm in materials science and engineering is the so-called *phase field method*. The technique has found increasing use by the materials community because of its fundamental origins and because it avoids some of the problems associated with sharp interface models. The phase field method introduces, along with the usual temperature field, an additional continuum field called the *phase field* or *order parameter*. This field assumes constant values in the bulk of each phase, continuously interpolating between its bulk values across a thin boundary layer, which is used to describe the interface between phases. From the

perspective of condensed matter physics, the phase field may be seen as describing the degree of crystallinity or atomic order or disorder in a phase. It can also be viewed as providing a fundamental description of an atomically diffuse interface. As a mathematical tool, the phase field can be seen as a tool that allows the interface to be smeared over a diffuse region for numerical expedience.

Traditional phase field models are connected to thermodynamics by a phenomenological free energy functional[1] written in terms of the phase field and other fields (temperature, concentration, strain, etc.). Through a dissipative minimization of this free energy, the dynamics of one or more order parameters, as well as those of heat or mass transfer, is governed by a set of nonlinear partial differential equations. Parameters of these dynamical equations of motion are tuned by association of the model – in the limit of a very small interface – with the associated sharp interface equations.

As will be explored in this book, phase field models, besides their fundamental thermodynamic connection, are exceedingly simple to program. They often do not require much more than a simple so-called Euler time marching algorithm on a uniform mesh (these will be examined later). For the more advanced users, more sophisticated techniques such as adaptive mesh refinement (AMR) and other rapid simulation schemes are also in abundance for free download and use these days.

The phase field methodology has become ubiquitous of late and is gaining popularity as a method of choice to model complex microstructures in solidification, precipitation, and strain-induced transformations. More recently, a new class of phase field models has also emerged, called *phase field crystal models*, which incorporate atomic scale elasticity alongside the usual phase transformation kinetics of traditional phase field models. Phase field crystal models are appealing as they will be shown to arise as special instances of *classical density functional theory*. This connection of phase field crystal models and classical density functional theory provides insight into the derivation of the effective constants appearing in phase field models from atomistic properties.

Of course, there are no free lunches! While phase field models might offer a deeper connection to fundamental thermodynamics than larger scale engineering or sharp interface models, they come with several severe problems that have traditionally stood in the way of making models amenable to quantitative modeling of experimentally relevant situations. For example, the emergence of a mesoscopic interface renders phase field equations very stiff. This requires multiscale numerical methods to resolve both the thin interfaces that are inherent in phase field models while at the same time capturing microstructures on millimeter–centimeter scales. Moreover, the numerical time steps inherent in phase field theory – limited by the interface kinetics – make it impossible to model realistic timescale. As a result, new mathematical techniques – thin interface asymptotic analysis methods – have to be

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1) A "functional" is a function whose input is an entire function rather than a single number. As a one-dimensional example, suppose a quantity f is dependent on a certain function of space $\phi(x)$. The quantity $F = \int f(\phi(x)) \, dx$ is then dependent on entire function $\phi(x)$ and is said to be a *functional* of $\phi(x)$. The functional dependence of F on $\phi(x)$ will be denoted by $F[\phi(x)]$.

developed that make it possible to accelerate numerical timescales without compromising solution quality. Luckily, recent advances on both these fronts – and others – have made it possible to overcome some of these challenges in selected problems. Understanding some of these methods and their application to the broader phase field methodology will be one of the main focuses of the chapters that follow.

References

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