This comprehensive and self-contained, one-stop source discusses phase-field methodology in a fundamental way, explaining complex mathematical and numerical techniques for solving phase-field and related continuum-field models. It also presents techniques used to model various phenomena in a detailed, step-by-step way, such that readers can carry out their own code developments.

Features many examples of how the methods explained can be used in materials science and engineering applications.

From the contents:
- Phase Transformation in Materials Science
- Elastic and Plastic Effects in Phase Transformations
- Modeling Atomic Scale Systems using the Phase-Field Method
- Numerical Solution Methods for simulating Phase-Field Models

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Phase-Field Methods in Materials Science and Engineering
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Preface

The idea for this book grew out of a series of workshops that took place at the McMaster University from 2002 to 2005 in which a couple of dozen researchers and students (called the Canadian Network for Computational Materials Science or CNCMS) were invited to discuss their research and their visions for the future of computational materials science. One serious concern that surfaced from the discussions and the proceedings regarded the gaping hole that existed in the standard pedagogical literature for teaching students – and professors – about computational and theoretical methods in phase field modeling. Indeed, unlike many other fields of applied physics and theoretical materials science, there is a dearth of easy-to-read books on phase field modeling that would allow students to come up to speed with the details of this topic in a short period of time. After sitting on the fence for a while, we decided to add our contribution by writing an introductory text about phase field modeling.

The aim of this book is to provide a graduate-level introduction of phase field modeling for students of materials science who wish to delve deeper into the underlying physics of the theory. The book begins with the basic principles of condensed matter physics to motivate and develop the phase field method. This methodology is then used to model various classes of nonequilibrium phase transformations that serve as paradigms of microstructure development in materials science phenomena. The workings of the various phase field models studied are presented in sufficient detail for students to be able to follow the reasoning and reproduce all calculations. The book also includes some basic numerical algorithms – accompanied by corresponding Fortran codes that come on a CD with this book – that students can use as templates with which to practice and develop their own phase field codes. A basic undergraduate-level knowledge of statistical thermodynamics and phase transformations is assumed throughout this book. Most long-winded mathematical derivations and numerical details that can serve as references but would otherwise detract from the flow of the main theme of the text are relegated to appendices.

It should be specified at the outset that this book is not intended to be an exhaustive survey of all the work conducted throughout the years with phase field modeling.
There are plenty of reviews that cover this angle and many of these works are cited in this book. Instead, we focus on what we feel is missing from much of the literature: a fast track to understanding some of the “dirty” details of deriving and analyzing various phase field models, and their numerical implementation. That is precisely what we have observed new students wishing to study phase field modeling are starved for as they get started in their research. As such, this book is intended to be a kind of “phase field modeling for dummies,” and so while the number of topics is limited, as many of the details as possible are provided for those topics that are covered.

The broad organization of the material in following chapters is as follows. The first half of the book begins by establishing the basic phase field phenomenology, from its basic origins in mean field theory of phase transformations to its basic form now in common use as the base of most modern phase field models in computational materials science and engineering. Phase field theory is applied to several examples, with a special emphasis placed on the paradigms of solidification and solid-state transformations. An appendix is also dedicated to the important issue of mapping the phase field model onto specific sharp interface limits. The last two chapters of this book deal with the development of more complex class of phase field models coined “phase field crystal” models. These are an extension of the original phase field formalism that makes it possible to incorporate elastic and plastic effects along side the usual kinetics that governs phase transformations. We will see that these models constitute a hybrid between traditional phase field theory and atomistic dynamics. After motivating the derivation of phase field crystal models from classical density functional theory, these models are then applied to various types of phase transformation phenomena that inherently involve elastic and plastic effects. It is noted that some sections of the book are marked as “Optional.” These are sections that can be skipped at first reading without losing the main flow of the text and without detracting from the minimum path of topics comprising the basic principles of phase field theory.

Writing this book involved the valued help of many people. We would like to thank all the graduate students in the Department of Materials Science and Engineering at the McMaster University who took MATLS 791 in the Fall of 2009. Their help and advice in editing and proofing the first edition of this book is greatly appreciated. I (NP) would like to thank my wife Photini and sons Spiro and Aristotle for their love and patience during the writing of this book; doing science for a living is fun but their love is what living is actually about. I also suppose thanks are in order to Starbucks Coffee for providing me – at the cost of lots of overpriced bitter coffee – many hours of escape from the mundane administrative environment of a modern university in order that I could work on this book in peace and talk politics with other patrons. I would also like to thank the Technical Research Centre of Finland (VTT) and the Helsinki University of Technology for hosting me during my sabbatical leave in 2009 and for flipping the bill for some of my travels to Helsinki where I also worked on this manuscript and other cool stuff.
As with anything in print, this book very likely contains typos and oversights. We would be delighted to hear from readers about any such errors or omissions. Please do not hesitate to contact us at provata@mcmaster.ca or elder@oakland.edu.

I (KE) would like to thank my wife Nancy, daughter Kate and parents Fay and Stan for the tremendous support they have given me over many years and throughout the writing of this text. In addition I would like to thank Tapio Ala-Nissila and the Helsinki University of Technology (now Aalto University) for providing me the opportunity to give several short courses on phase field and phase field crystal modelling. Some of the material developed for those courses has found its way into the text.

_Nikolas Provatas_

_Ken Elder_
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](image.jpg)

**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.
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 1.2](image)

**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).*

...
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:

\[
\begin{align*}
\frac{\partial T}{\partial t} &= \nabla \cdot \left( \frac{k}{\rho c_p} \nabla T \right) \\
\rho L_f V_n &= k_s \nabla T \cdot \vec{n}^s_{\text{int}} - k_l \nabla T \cdot \vec{n}^l_{\text{int}} \\
T_{\text{int}} &= T_m - \left( \frac{\gamma T_m}{L_f} \right) \kappa - \frac{V_n}{\mu}
\end{align*}
\]

(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), \( \rho \) the density of the solid and
liquid, \( c_p \) the specific heat at constant pressure, \( \alpha \) the thermal diffusion coefficient, \( L_f \) the latent heat of fusion for solidification, \( \gamma \) the solid–liquid surface energy, \( T_M \) the melting temperature, \( \kappa \) the local solid–liquid interface curvature, \( V_n \) the local normal velocity of the interface, and \( \mu \) 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

\(^1\) 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

Mean Field Theory of Phase Transformations

The origins of the phase field methodology – the focus of this book – have been considerably influenced by mean field theory of first- and second-order phase transformations. It is thus instructive to begin first with a discussion of some simple phase transformations and their description via mean field theory. Using this as a framework will better allow the concept of an order parameter to be defined and generalized to include spatial variations. This will thus set the stage for the later development of phase field models of solidification and solid-state transformation phenomenon. Before proceeding, the reader should have a basic background of statistical thermodynamics. For a quick review, the reader may refer to Refs [1–3].

Common first-order transformations include solidification of liquids and condensation of vapor. They are defined by a release of latent heat and discontinuous first derivative of the free energy. Moreover, just below a first-order transformation, nucleation of the metastable phase is required to initiate the transformation. Finally, in first-order transformations, two phases can typically coexist over a wide range of temperatures, densities (pure materials), or impurity concentrations (alloys). In contrast, second-order transformations occur at well-defined temperature, density, or concentration. There is no release of latent heat and the transformation begins spontaneously due to thermal fluctuations. A paradigm example is phase separation of a binary mixture or spinodal decomposition in metal alloys. Another is the spontaneous ferromagnetic magnetization of iron below its Currie temperature.

An important concept used again and again in the description of phase transformations is that of the order parameter. This is a quantity that parameterizes the change of symmetry from the parent (disordered) phase to the daughter (ordered) phase appearing after the transformation. For example, a crystal phase has fewer rotational and translational symmetries compared to a liquid. The order parameter typically takes on a finite value in the ordered state and vanishes in the disordered state. First- and second-order phase transitions are distinguished by the way the order parameter appears below the transition temperature. In a first-order transformation, the order parameter of the ordered state emerges discontinuously from that of the disordered phase, below the transformation temperature. In the second-order transformation, the disordered state gives way continuously to two ordered phases with nonzero order parameter. Another example of a change of symmetry characterized by changes in the...
order parameter includes the average magnetization. For some phase changes, such as vapor $\rightarrow$ vapor + liquid, there is no change in the structural symmetry groups of the parent and daughter phases. In such case, effective order parameters can often be defined in terms of density differences relative to the parent phase.

Mean field theory of phase transformations ignores spatial fluctuations, which always exist due to local molecular motion. The order parameter – treated as an average thermodynamic property of a phase – is used to write the free energy of a system. Its subsequent thermodynamic properties can thus be determined. This approach works reasonably well in first-order transformations, where fluctuations influence only regions near nanoscale phase boundaries, even near the transition temperature. In contrast, second-order transformation fluctuations influence ordering over increasing length scales, particularly near a critical point. For such problems, spatial fluctuations play a dominant role and mean field Landau free energy functional must be augmented with terms describing spatial fluctuations. These are also written in terms of gradients of the order parameter, which in this case is considered to be varying spatially on scales over which spatial fluctuations occur.

This chapter begins by illustrating two phenomenological microscopic models that help motivate and define the concept of an order parameter and mean field treatments of phase transformations.

2.1 Simple Lattice Models

2.1.1 Phase Separation in a Binary Mixture

Consider a binary mixture of two components A and B. Imagine the domain on which the mixture is broken into many small discrete volume elements labeled with the index $i$. Each element contains either one A or one B atom. The total number of cells $M$ equals the total number of atoms $N$, a definition valid for an incompressible fluid mixture. For each cell $1 < i < N$, a state variable $n_i$ is defined, which takes on $n_i = 0$ if a volume element is occupied by an A atom and $n_i = 1$ when it is occupied by a B atom. The variable $n_i$ thus measures the local concentration of B atoms in each cell. The total number of unique states of the system is given by $2^N$, where each configurational state is denoted by the notation $\{n_i\}$. Assuming that each particle interacts with $v$ of its neighbors, the total interaction energy of a particular configuration of the binary mixture is given by

$$E[\{n_i\}] = -\sum_{i=1}^{N} \sum_{j=1}^{v} \{\epsilon_{AA}(1-n_i)(1-n_j) + \epsilon_{AB}(1-n_i)n_j + \epsilon_{AB}(1-n_j)n_i + \epsilon_{BB}n_in_j\}$$

(2.1)

This expression can be simplified by interchanging the $i$ and $j$ subscripts and noting that $n_in_j = n_i - n_i(1-n_j)$, which gives
\[ E(\{n_i\}) = \varepsilon \sum_{i=1}^{N} \sum_{j=1}^{N} n_i(1-n_j) + b \sum_{i=1}^{N} n_i \frac{N \varepsilon_{AA}}{2} \]  

(2.2)

where \( \varepsilon = \varepsilon_{AA} + \varepsilon_{BB} - 2 \varepsilon_{AB} \) and \( b = (\mathcal{V}/2)(\varepsilon_{AA} - \varepsilon_{BB}) \).

The thermodynamics of this simple system is described by the grand potential [1]

\[ \Omega(\mu, N, T) = F(N, \langle N_B \rangle, T) - \mu \langle N_B \rangle \]  

(2.3)

where \( \mu \) is the chemical potential of the system and

\[ \langle N_B \rangle \equiv \left\langle \sum_{i=1}^{N} n_i \right\rangle \]  

(2.4)

is the average concentration of B particles. The free energy per particle can be expressed as

\[ f = \frac{F(\phi, N, T)}{N} = \frac{\Omega(\mu, N, T)}{N} + \mu \phi \]  

(2.5)

where \( \phi \) is the order parameter, defined by

\[ \phi = \frac{1}{N} \left\langle \sum_{i=1}^{N} n_i \right\rangle \equiv \langle n_i \rangle \]  

(2.6)

Equation 2.5 makes explicit the dependencies of the free energy density on the chemical potential and the order parameter of the system, which in this case is the average concentration of B atoms.

From the principles of statistical mechanics, the free energy \( f \) in Equation 2.5 can be connected to the interaction energy in Equation 2.1 via the grand partition function \( \Xi \), which determines the grand potential \( \Omega \) according to

\[ \Omega = -k_B T \ln \Xi \]  

(2.7)

where \( k_B \) is the Boltzmann constant and

\[ \Xi = \prod_{i=1}^{N} \sum_{n_i=0,1} e^{-\beta(E(\{n_i\})-\mu n_i)} \]  

(2.8)

where \( \beta \equiv 1/k_B T \) and \( N_B = \sum_{i=1}^{N} n_i \). Equation 2.8 represents a configurational sum of the Boltzmann factor over all \( 2^N \) configurations of the binary mixture. The order parameter in Equation 2.6 can be directly evaluated from the grand partition function equation(2.8), or from Equation 2.5, according to

\[ \phi = -\frac{1}{N} \frac{\partial \Omega}{\partial \mu} \bigg|_{N,T} \]  

(2.9)

The configurational sum in Equation 2.8 cannot be performed for most complex interacting systems including the simple binary mixture model presented here. Nevertheless, a considerable insight into the thermodynamics of this lattice model
can be gleaned by making some simplification on the interaction terms. Namely, we invoke mean field approximation, which assumes that the argument of the Boltzmann factor in the configurational sum of $\Xi$ can be replaced by its mean or equilibrium value. The implication of this assumption is that the main contribution to $\Xi$ comes from particle configurations close to those that minimize the argument of the Boltzmann factor in $\Xi$. Thus, in mean field theory the partition function becomes

$$\Xi \approx \prod_{i=1}^{N} \sum_{n_i=0.1} e^{-\beta(E[n_i]) + \mu\beta(N_i)}$$

$$= \frac{N!}{(N_B!)!(N-(N_B))!} e^{-\beta(E[n_i]) + \mu\beta(N_i)}$$

(2.10)

Accordingly, the grand potential in mean field theory becomes

$$\Omega = -k_B T \ln \Xi$$

$$\approx -k_B T \ln \left( \frac{N!}{(N_B!)!(N-(N_B))!} \right) + \langle E[n_i] \rangle - \mu \langle N_B \rangle$$

(2.11)

The mean energy $E[n_i]$ per particle can be written as

$$\frac{\langle E[n_i] \rangle}{N} = \frac{\epsilon}{N} \sum_{i=1}^{N} \sum_{j=1}^{\nu} \langle n_i \rangle (1-\langle n_i \rangle) + \frac{b}{N} \sum_{i=1}^{N} n_i - \frac{\nu \epsilon_{AA}}{2}$$

$$= \frac{\nu \epsilon}{2} \phi (1-\phi) + b\phi - \frac{\nu \epsilon_{AA}}{2}$$

(2.12)

Equation 2.12 and use of Sterling’s approximation makes it possible to finally write the mean field free energy density $f$ in Equation 2.5 for the binary mixture in terms of the order parameter as

$$f = \frac{\nu \epsilon}{2} \phi (1-\phi) + b\phi - \frac{\nu \epsilon_{AA}}{2} + k_B T \left\{ \phi \ln \phi + (1-\phi)\ln(1-\phi) \right\}$$

(2.13)

Figure 2.1 shows the free energy in Equation 2.13 for several temperatures above and below the critical value below which one stable state of concentration continuously gives way to two. It is assumed in this figure that $\epsilon_{AA} = \epsilon_{BB}$ and $\nu = 4$; that is, the alloy is two dimensional. The free energy wells in the figure correspond to free energies of individual phases. Since impurity concentration (i.e., number of B atoms) is conserved, the order parameter in this problem is referred to as conserved. It will be seen that this designation has important implications for the type of dynamical equations that can be written for the spatial evolution of $\phi$ (or other conserved order parameters).

Since the order parameter represents a concentration – a conserved quantity – we can apply the standard Maxwell equal area construction [4, 5] to calculate the stable or equilibrium states of concentration the system can take below the critical temperature (i.e., the phase diagram). This construction leads to the so-called “common
tangent construction,” in which one graphically connects the free energy wells of any two phases by a common tangent line. The points where this tangent intersects the free energy wells determine the equilibrium concentrations $w_{eq}$ of the coexisting alloy phases. The slope of the line corresponds to the equilibrium chemical potential of the system, also expressed as $m_{eq} = \frac{\partial f}{\partial \phi}_{w_{eq}}$. From the simple form of the free energy curves in Figure 2.1, the equilibrium chemical potential can be seen to satisfy $m_{eq} = 0$. Thus, the equilibrium concentrations $w_{eq}$ are found by solving

$$m_{eq} = \frac{\partial f}{\partial \phi}_{w_{eq}} = 0 \quad (2.14)$$

Substituting Equation 2.13 into Equation 2.14 gives the transcendental equation

$$w_{eq} = \frac{1}{2} \tanh \left( \frac{\epsilon v}{2k_B T} \left( w_{eq} - \frac{1}{2} \right) \right) \quad (2.15)$$

Solutions of Equation 2.15 exist only for $T < T_c = \epsilon v / 4k_B$, which defines the critical temperature for this alloy. This form of free energy is such that below a critical temperature two states emerge continuously from one. This means that at a temperature arbitrarily close to (and below) $T_c$, the two stable states $\phi_{eq}$ are arbitrarily close to the value $\phi_{eq} = 0$ above $T_c$. This type of behavior is typical of a second-order phase transformation.

2.1.2 Ising Model of Magnetism

A second microscopic system that can be described in terms of a well-defined order parameter is a collection of magnetic spins in an external magnetic field. Consider
a domain of atoms, each of which carries a magnetic spin $s_i = \pm 1$, that is, the atoms’ magnetic moment points up or down. The energy of this system of spins is given by

$$E\{s_i\} = -\sum_{i=1}^{N} \sum_{j=1}^{\nu} J s_i s_j - B \sum_{i=1}^{N} s_i$$  \hspace{1cm} (2.16)$$

where $\nu$ represents the nearest neighbors of each spin. The first term of Equation 2.16 sums up the interaction energies of each spin (i) with all other spins (j). The second term adds the energy of interaction of each spin with an externally imposed magnetic field. In this system, the order parameter is defined as

$$\phi = \frac{1}{N} \left\langle \sum_{i=1}^{N} s_i \right\rangle \equiv \langle s_i \rangle$$  \hspace{1cm} (2.17)$$

which represents the average magnetization of the system. Unlike the case of the binary alloy where the average concentration of B atoms relative to the total number of atoms in the system was conserved, the average magnetization is not a conserved quantity.

The statistical thermodynamics of this system can be considered via the canonical partition function for an $N$-spin system (since the number of spins is assumed not to change), given by

$$Q = \prod_{i=1}^{N} \sum_{s_i = -1,1} e^{-\beta E(s_1, s_2, s_3, ..., s_N)}$$  \hspace{1cm} (2.18)$$

One of the primary premises of statistical mechanics is that the partition function can be used to calculate the free energy per spin, according to

$$f = -\frac{k_B T}{N} \ln Q$$  \hspace{1cm} (2.19)$$

From Equations 2.18 and 2.19, the order parameter defined by Equation 2.17 can be evaluated as

$$\phi = \frac{1}{Q} \prod_{i=1}^{N} \sum_{s_i = -1,1} \left( \frac{1}{N} \sum_{i=1}^{N} s_i \right) e^{-\beta \left( -B \sum_{i=1}^{N} s_i - J \sum_{i=1}^{N} \sum_{j=1}^{\nu} s_i s_j \right)}$$

$$= \frac{\partial((k_B T/N) \ln Q)}{\partial B}$$  \hspace{1cm} (2.20)$$

$$= -\frac{\partial f}{\partial B}$$

Note that the use in the binary alloy example of the grand canonical ensemble, where particle number varies, was used for convenience. We would have obtained the same results if we used the canonical ensemble where particle number remains fixed.