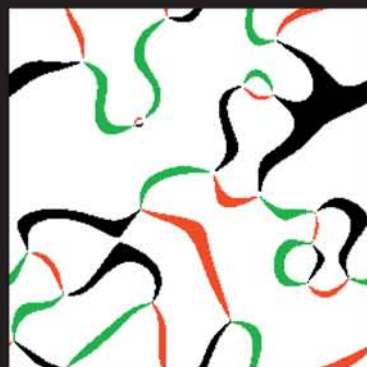
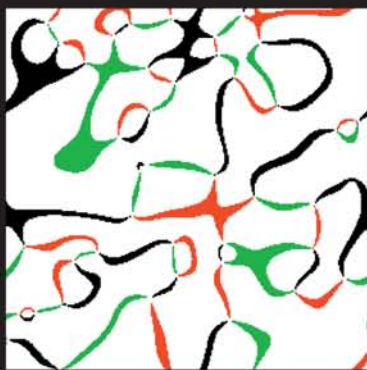




# KINETICS of PHASE TRANSITIONS

Edited by  
**Sanjay Puri and  
Vinod Wadhawan**



**CRC Press**  
Taylor & Francis Group

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10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-0-8493-9065-4 (Hardcover)

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**Library of Congress Cataloging-in-Publication Data**

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Kinetics of phase transitions / [edited by] Sanjay Puri, Vinod Wadhawan.  
p. cm.

Includes bibliographical references and index.

ISBN 978-0-8493-9065-4 (hardcover : alk. paper)

1. Phase transformations (Statistical physics) 2. Phase rule and equilibrium. 3.

Materials--Thermal properties. I. Puri, Sanjay, 1962- II. Wadhawan, Vinod K. III.  
Title.

QC175.16.P5K56 2009  
530.4'74--dc22

2008054120

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# Preface

This book focuses on the kinetics of phase transitions, that is, the evolution of a system from an unstable or metastable state to its preferred equilibrium state. A system may become thermodynamically unstable due to a sudden change in external parameters like temperature, pressure, magnetic field, and so on. The subsequent dynamics of the far-from-equilibrium system is usually nonlinear and is characterized by complex spatiotemporal pattern formation. Typically, the system evolves toward its new equilibrium state via the emergence and growth of domains enriched in the preferred state. This process is usually referred to as phase-ordering dynamics or domain growth or coarsening. There has been intense research interest in this field over the past few decades, as the underlying physical processes are of great scientific and technological importance. Problems in this field arise from diverse disciplines such as physics, chemistry, metallurgy, materials science, and biology. As a result of this research activity, our understanding of phase-ordering dynamics has reached a high level of sophistication. At the same time, many challenging problems continue to arise in different contexts. It is now clear that the paradigms and concepts of phase-ordering dynamics are of much wider applicability than was initially thought.

In the context of the above developments, we believed that there was a strong need for a book that summarizes our current understanding of domain growth. Furthermore, we believed that this book should be written at a level accessible to the advanced undergraduate; that is, it should be a textbook rather than an advanced research monograph. With this in mind, we wrote to various leaders in this field with a request to each to contribute a chapter. Their responses were very positive, and this book is an outcome of the collective efforts of various colleagues. On our part, we have edited and homogenized the various chapters so that this book reads as a seamless “multiple-author book” rather than as the usual disjointed “edited book.”

Let us provide an overview of the various chapters. The first chapter (written by Sanjay Puri) provides an overview of studies of domain growth in simple systems. This chapter develops the theoretical tools and methodology that are used in subsequent chapters. The second chapter (written by Kurt Binder) focuses on the distinction between spinodal decomposition and nucleation and growth, which are common scenarios for domain growth problems. This issue has been discussed extensively in the literature, but there remains considerable confusion over the interpretation of various experiments and simulations. Kurt Binder addresses this issue in great detail, emphasizing that there is no sharp boundary between spinodal decomposition and nucleation.

Chapters 3 and 4 are dedicated to a discussion of simulation techniques in this field. In Chapter 3, Gerard Barkema describes Monte Carlo simulations of kinetic Ising models. In Chapter 4, Giuseppe Gonnella and Julia Yeomans discuss lattice



Boltzmann simulations, which have proved very useful in understanding the late stages of phase separation in fluid mixtures. Numerical simulations have played a crucial role in developing our understanding of phase-ordering dynamics. The methodology described in Chapters 3 and 4 will prove very useful for a researcher entering this field.

In Chapter 5, Marco Zannetti discusses slow relaxation and aging in phase-ordering systems. These phenomena are well known in the context of structural glasses and spin glasses. Recent studies indicate that these concepts are also highly relevant in domain growth problems—Zannetti provides an overview of these studies.

Recent interest in this area has focused on incorporating various experimentally relevant features in studies of phase-ordering systems. In this context, Chapter 6 (by Rajesh Khanna, Narendra Kumar Agnihotri, and Ashutosh Sharma) describes the kinetics of dewetting of liquid films on surfaces. In Chapter 7, Takao Ohta reviews studies of phase separation in diblock copolymers. In these systems, the segregating polymers are jointed, so that the system can only undergo phase separation on micro-scales.

Finally, in Chapter 8 (written by Akira Onuki, Akihiko Minami, and Akira Furukawa), there is a discussion of phase separation in solids. Strain fields play an important role in the segregation kinetics of alloys. Onuki et al. discuss how elastic fields can be incorporated into the description of segregation in solid mixtures.

Before we conclude, it would be appropriate to thank those who have contributed to this project. First, we are grateful to the authors, who have made the effort to write pedagogical reviews of various research problems. Second, we wish to thank our colleagues and collaborators, who have contributed so much to our understanding and appreciation of this fascinating field of research. Finally, we are grateful to the editorial and production staff at CRC Press/Taylor & Francis for their assistance in getting this book into its final form.

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# Editors

**Professor Sanjay Puri** is an expert in the fields of statistical physics and nonlinear dynamics. He has made important contributions to these fields and has published two books and more than 125 papers. His publications have been extensively cited, and he is an established authority in the kinetics of phase transitions. Dr. Puri received an MS degree in physics in 1982 from the Indian Institute of Technology, Delhi, and a PhD degree in physics in 1987 from the University of Illinois at Urbana-Champaign. In 1987, he joined the School of Physical Sciences at Jawaharlal Nehru University, New Delhi, and has been there ever since. He has received many awards and honors for his research achievements. For example, in 2006 he was elected a fellow of the Indian Academy of Sciences, Bangalore. In 2006, he also received the prestigious Shanti Swarup Bhatnagar Prize from the Government of India.

**Dr. Vinod Wadhawan** is a condensed-matter physicist with special interest in ferroic materials, phase transitions, and the utilitarian role of symmetry considerations in materials science. He introduced the important notion of “latent symmetry” in composite systems. He has edited/coedited 10 volumes on various aspects of phase transitions and has written two books: one on ferroic materials (the first definitive book on the subject) and the other on smart structures. Dr. Wadhawan received his MSc degree in physics from the University of Delhi in 1967, and a PhD degree from the University of Bombay in 1976. He has been with the Department of Atomic Energy, Government of India, since then—he currently holds the prestigious Raja Ramanna Fellowship at Bhabha Atomic Research Centre, Mumbai. Dr. Wadhawan is an associate editor of *Phase Transitions* (Taylor & Francis), a journal with which he has been associated since 1985. He is also a recipient of the Materials Research Society of India medal.



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# 1 Kinetics of Phase Transitions

*Sanjay Puri*

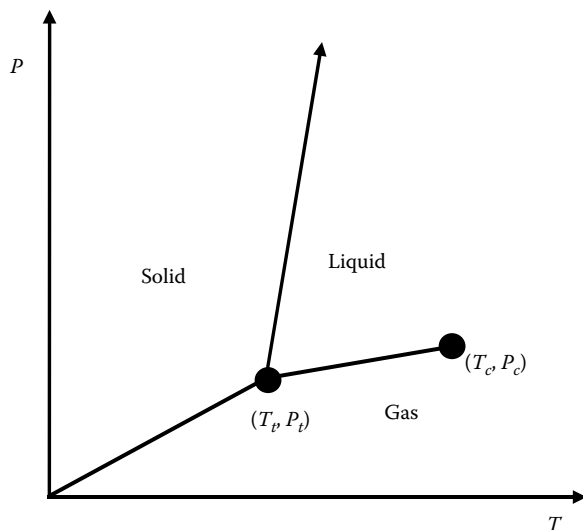
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## 1.1 INTRODUCTION

Many systems exist in multiple phases, depending on the values of external parameters, for example, temperature ( $T$ ), pressure ( $P$ ), and so on. In this context, consider a fluid (e.g., water), which can exist in three phases, viz., liquid, solid, and gas. The phase diagram of this fluid in the  $(T, P)$ -plane is shown in Figure 1.1. The chosen phase at a particular  $(T, P)$ -value is the one with lowest Gibbs potential  $G(T, P)$ . This phase diagram is characterized by a range of fascinating features, for example, lines of first-order phase transitions, a second-order critical point, a triple point, and so on. The correct understanding of these features is of great scientific and technological importance. We have gained a thorough understanding of the equilibrium aspects of phase transitions (and phase diagrams) through many important works, starting with the seminal contribution of Van der Waals [1,2].

There is also a fascinating class of problems involving the *kinetics of phase transitions*, that is, the evolution dynamics of a system that is rendered thermodynamically unstable by a rapid change of parameters. In the context of Figure 1.1, consider a situation in which the fluid in the solid phase is rapidly heated to a temperature where the preferred equilibrium state is the liquid phase. Clearly, the solid will convert to liquid on some timescale, so the initial and final states of the system are well understood. However, we have less knowledge about the dynamical processes that occur as the solid converts to liquid. These processes play a crucial role in our everyday life. Over the years, our understanding of the kinetics of phase transitions has improved greatly [3–6]. This book provides an overview of developments in this area.

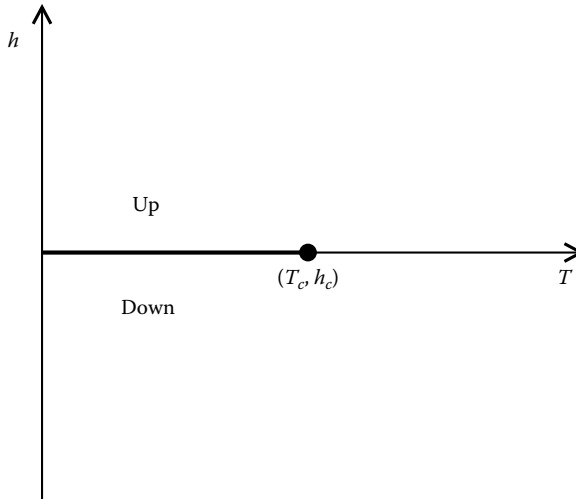


**FIGURE 1.1** Phase diagram of a fluid in the  $(T, P)$ -plane. The system can exist in either of three phases—liquid, gas, or solid. The solid lines denote lines of first-order phase transitions. At the triple point  $(T_t, P_t)$ , all three phases coexist. The point labeled  $(T_c, P_c)$  is the critical point of the system.

Before we proceed, it is relevant to develop the appropriate terminology first. One is often interested in the evolution of systems whose parameters have been drastically changed. Such systems are referred to as *far-from-equilibrium systems*, and their evolution is characterized by *nonlinear evolution equations* and *spatiotemporal pattern formation*. In most cases, we are unable to obtain exact solutions for the time-dependent evolution of the system. However, the presence of *domain boundaries* or *defects* in these systems provides a convenient analytical tool to understand the resultant pattern dynamics.

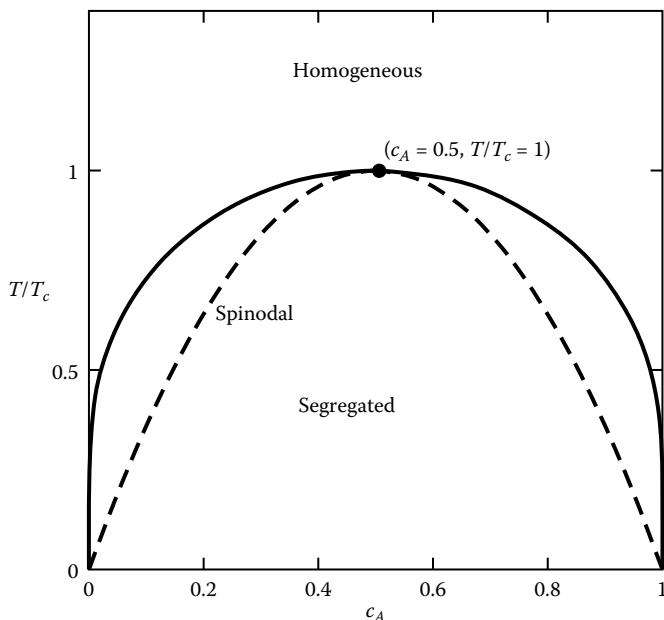
Let us consider two other problems in this context. These will serve as paradigms for understanding the kinetics of phase transitions. First, consider a ferromagnet whose phase diagram is shown in Figure 1.2. Focus on the case with zero magnetic field ( $h = 0$ ). At high temperatures, the magnet is in a disordered or paramagnetic state. If the temperature is suddenly quenched to  $T < T_c$ , this system now prefers to be in the magnetized state with spins pointing in the “up” or “down” directions. The evolution of the system is characterized by the emergence and growth of domains enriched in either up or down spins. As time  $t \rightarrow \infty$ , the system approaches a spontaneously magnetized state.

Second, consider a binary (AB) mixture whose phase diagram is shown in Figure 1.3. The system is mixed or homogeneous at high temperatures. At time  $t = 0$ , the mixture is suddenly quenched below the *coexistence curve* or *miscibility gap*. This system now prefers to be in the phase-separated state and proceeds to its equilibrium state via the growth of domains that are either A-rich or B-rich. The nonequilibrium dynamics of the magnet or binary mixture is usually referred to as *domain growth* or *coarsening* or *phase-ordering kinetics*.



**FIGURE 1.2** Phase diagram of a ferromagnet. The system parameters are the temperature ( $T$ ) and the magnetic field ( $h$ ). The point  $(T_c, h_c = 0)$  is a second-order critical point. The line  $(T < T_c, h = 0)$  corresponds to a line of first-order transitions. At low temperatures ( $T < T_c$ ), the system can be in either of two phases, up or down, depending on the orientation of the magnetic spins.





**FIGURE 1.3** Phase diagram of a binary (AB) mixture. The system parameters are the concentration of A ( $c_A = 1 - c_B$ ) and the temperature ( $T$ ). The point ( $c_A = 0.5, T/T_c = 1$ ) corresponds to a second-order critical point. Above the coexistence curve (solid line), the system is in a homogeneous or disordered state. Below the coexistence curve, the system is in a segregated or phase-separated state, characterized by A-rich and B-rich regions. The dashed lines denote spinodal curves. The homogeneous system is metastable between the coexistence and spinodal curves and unstable below the spinodal lines.

There have been many studies of the kinetics of phase transitions. Problems in this area arise in diverse contexts, ranging from *clustering dynamics in the early universe* to the *growth of nanostructures*. This book is a pedagogical exposition of developments in this area and is organized as follows. This chapter reviews the framework of phase-ordering kinetics and develops the tools and terminology used in later chapters. The subsequent chapters are written by leading experts in this area and focus on problems of special interest in the context of phase-ordering dynamics. All the chapters are written in textbook style and are accessible at the level of the advanced undergraduate student. At this point, we should stress that our understanding of this area has been greatly facilitated by numerical simulations of appropriate models. Therefore, two chapters of this book are dedicated to tutorial-level discussions of numerical simulations in this field. The first of these is written by Barkema (Chapter 3)—this chapter focuses on Monte Carlo simulations of *kinetic Ising models*. The second of these is written by Gonnella and Yeomans (Chapter 4) and describes the application of *lattice Boltzmann algorithms* to study phase-ordering systems.

This chapter is organized as follows. In Section 1.2, we introduce the Ising model for two-component mixtures and study its equilibrium properties in the mean-field (MF) approximation. This will enable us to obtain the phase diagrams shown in

Figures 1.2 and 1.3. In Section 1.3, we study kinetic versions of the Ising model. In Section 1.4, we discuss domain growth with a *nonconserved order parameter*, for example, ordering dynamics of a ferromagnet into up and down phases. In this section, we separately examine cases with scalar and vector order parameters. In Section 1.5, we discuss domain growth with a *conserved order parameter*, for example, kinetics of phase separation of an AB mixture. We will separately focus on segregation in binary alloys that is driven by diffusion, and segregation in binary fluids where flow fields drastically modify the asymptotic behavior. Finally, Section 1.6 concludes this chapter with a summary and discussion.

## 1.2 PHASE DIAGRAMS OF TWO-COMPONENT MIXTURES

### 1.2.1 ISING MODEL AND ITS APPLICATIONS

The simplest model of an interacting many-body system is the Ising model [7], which was first introduced as a model for phase transitions in magnetic systems. However, with suitable generalizations, it has wide applications to diverse problems in condensed matter physics.

Consider a set of  $N$  spins  $\{S_i\}$ , which are fixed on the sites  $\{i\}$  of a lattice. The two-state (spin-1/2) Ising Hamiltonian has the following form:

$$H = -J \sum_{\langle ij \rangle} S_i S_j, \quad S_i = \pm 1, \quad (1.1)$$

where  $J$  is the strength of the exchange interaction between spins. We consider the case with nearest-neighbor interactions only, denoted by the subscript  $\langle ij \rangle$  in Equation 1.1.

Although the Hamiltonian in Equation 1.1 is formulated for a magnetic system, it is clear that a similar description applies for any interacting two-state system, as the two states can be mapped onto  $S = +1$  or  $-1$ . A well-known example is the lattice gas or binary (AB) mixture [7]. We can describe this system in terms of occupation-number variables  $n_i^\alpha = 1$  or  $0$ , depending on whether or not a site  $i$  is occupied by species  $\alpha$  (A or B). Clearly,  $n_i^A + n_i^B = 1$  for all sites. A more convenient description is obtained in terms of spin variables  $S_i = 2n_i^A - 1 = 1 - 2n_i^B$ . We associate an interaction energy  $-\epsilon_{\alpha\beta}$  between species  $\alpha$  and  $\beta$ , located at neighboring sites  $i$  and  $j$ , respectively. The corresponding Hamiltonian is

$$\begin{aligned} H &= - \sum_{\langle ij \rangle} \left[ \epsilon_{AA} n_i^A n_j^A + \epsilon_{BB} n_i^B n_j^B + \epsilon_{AB} (n_i^A n_j^B + n_i^B n_j^A) \right] \\ &= - \left( \frac{\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}}{4} \right) \sum_{\langle ij \rangle} S_i S_j - \frac{q(\epsilon_{AA} - \epsilon_{BB})}{4} \sum_{i=1}^N S_i \\ &\quad - \frac{Nq}{8} (\epsilon_{AA} + \epsilon_{BB} + 2\epsilon_{AB}). \end{aligned} \quad (1.2)$$

In Equation 1.2,  $q$  denotes the coordination number of a lattice site. The second term on the right-hand side (RHS) is constant because  $\sum_i S_i = N_A - N_B$ , where  $N_\alpha$  is the

number of  $\alpha$ -atoms in the system. Further, the third term on the RHS is also a constant. The Hamiltonian in Equation 1.2 is analogous to that in Equation 1.1 if we identify

$$J = \frac{\epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}}{4}. \quad (1.3)$$

The Ising model and its variants are not restricted to two-state systems and can be easily generalized to the case of multiple-state systems. Thus, three-state systems can be mapped onto a spin-1 Hamiltonian; four-state systems onto a spin-3/2 Hamiltonian; and so on. In general, higher-spin models have a larger number of possible interaction terms (and parameters) in the Hamiltonian.

We can obtain phase diagrams for magnets (cf. Figure 1.2) and binary mixtures (cf. Figure 1.3) by studying the Ising model in the mean-field (MF) approximation, as described below.

### 1.2.2 PHASE DIAGRAMS IN THE MEAN-FIELD APPROXIMATION

The equilibrium properties of the Ising model in Equation 1.1 are described in the MF approximation by the Bragg–Williams (BW) form of the Gibbs free energy [7]. This is obtained as follows. Consider a homogeneous state with spatially uniform magnetization  $\langle S_i \rangle = \psi$ . We approximate the energy as

$$E(\psi) \simeq -J \sum_{\langle ij \rangle} \langle S_i \rangle \langle S_j \rangle = -\frac{NqJ}{2} \psi^2. \quad (1.4)$$

The corresponding probabilities for a site to have up ( $\uparrow$ ) or down ( $\downarrow$ ) spins are

$$\begin{aligned} p_{\uparrow} &= \frac{1 + \psi}{2}, \\ p_{\downarrow} &= \frac{1 - \psi}{2}. \end{aligned} \quad (1.5)$$

Therefore, the entropy for a lattice with  $N$  sites is

$$S(\psi) = -Nk_B \left[ \left( \frac{1 + \psi}{2} \right) \ln \left( \frac{1 + \psi}{2} \right) + \left( \frac{1 - \psi}{2} \right) \ln \left( \frac{1 - \psi}{2} \right) \right], \quad (1.6)$$

where  $k_B$  is the Boltzmann constant.

Then, the Gibbs free energy is obtained as

$$G(\psi) = E(\psi) - hM - TS(\psi), \quad (1.7)$$

where  $h$  is the magnetic field, and  $M (=N\psi)$  is the overall magnetization.

This yields the free energy per spin as

$$\begin{aligned}
 g(T, h, \psi) &= \frac{G(T, h, \psi)}{N} \\
 &= -\frac{1}{2}qJ\psi^2 - h\psi \\
 &\quad + k_B T \left[ \left( \frac{1+\psi}{2} \right) \ln \left( \frac{1+\psi}{2} \right) + \left( \frac{1-\psi}{2} \right) \ln \left( \frac{1-\psi}{2} \right) \right].
 \end{aligned} \tag{1.8}$$

The RHS of Equation 1.8 is a variational function of the magnetization  $\psi = \langle S_i \rangle$ . If we Taylor-expand the entropy term in Equation 1.8, the Gibbs free energy assumes the customary  $\psi^4$ -form:

$$g(T, h, \psi) = \frac{1}{2} (k_B T - qJ) \psi^2 - h\psi + \frac{k_B T}{12} \psi^4 + O(\psi^6) - k_B T \ln 2. \tag{1.9}$$

The order parameter  $\psi$  in Equation 1.8 or Equation 1.9 can describe both ferromagnetic and antiferromagnetic order, with  $J < 0$  in the latter case. Furthermore, in the antiferromagnetic case,  $\psi$  refers to the *sublattice magnetization* or *staggered magnetization* [7].

The equilibrium value of  $\psi$  at fixed  $(T, h)$  is obtained from Equation 1.8 by minimizing the Gibbs free energy:

$$\left. \frac{\partial g}{\partial \psi} \right|_{\psi=\psi_0} = 0. \tag{1.10}$$

This yields the well-known transcendental equation [ $\beta = (k_B T)^{-1}$ ]:

$$\psi_0 = \tanh(\beta qJ\psi_0 + \beta h). \tag{1.11}$$

For  $h = 0$ , we identify the MF critical temperature

$$T_c = \frac{qJ}{k_B}. \tag{1.12}$$

For  $T > T_c$  and  $h = 0$ , the transcendental equation has only one solution  $\psi_0 = 0$ , which corresponds to the paramagnetic state. For  $T < T_c$ , Equation 1.11 has three solutions  $\psi_0 = 0, \pm\psi(T)$ . The state with  $\psi_0 = 0$  has a higher free energy than do the equivalent states  $+\psi(T)$  and  $-\psi(T)$ . Further,  $\psi(T) \rightarrow 1$  as  $T \rightarrow 0$ , and  $\psi(T) \rightarrow 0$  as  $T \rightarrow T_c^-$ . The relevant phase diagram in the  $(T, h)$ -plane is shown in Figure 1.2.

Next, let us consider the case of the binary mixture (or lattice gas) with  $N_A (=c_A N)$  atoms of species A and  $N_B (=c_B N)$  atoms of species B ( $N = N_A + N_B$ ). The appropriate order parameter in this case is the local density difference,  $\psi = \langle n_i^A \rangle - \langle n_i^B \rangle$ . The above analysis has to be modified because the appropriate ensemble for a binary

mixture is characterized by a fixed *magnetization* rather than a fixed *magnetic field*. The relevant free energy to be minimized is the Helmholtz potential

$$F(T, \psi) = E(\psi) - TS(\psi). \quad (1.13)$$

For the BW free energy, we have the expression

$$\begin{aligned} f(T, \psi) &= \frac{F(T, \psi)}{N} \\ &= -\frac{1}{2}qJ\psi^2 + k_B T \left[ \left( \frac{1+\psi}{2} \right) \ln \left( \frac{1+\psi}{2} \right) + \left( \frac{1-\psi}{2} \right) \ln \left( \frac{1-\psi}{2} \right) \right]. \end{aligned} \quad (1.14)$$

For a system that undergoes phase separation, there are two possibilities:

- (a) We can have a *homogeneous* (or one-phase) state with order parameter  $\psi_h = c_A - c_B$ .
- (b) We can have a *phase-separated* state where the system segregates into two regions having order parameter  $\psi_1$  (with fraction  $x$ ) and  $\psi_2$  [with fraction  $(1-x)$ ]. The quantity  $x$  is determined from the lever rule

$$\psi_h = x\psi_1 + (1-x)\psi_2. \quad (1.15)$$

Let us minimize the Helmholtz potential  $\bar{f}$  for the phase-separated state. (The homogeneous state is the limit  $\psi_1 = \psi_2$ .) The quantity  $\bar{f}$  is obtained as

$$\bar{f} = xf(\psi_1) + (1-x)f(\psi_2). \quad (1.16)$$

This has to be minimized subject to the constraint in Equation 1.15. We implement this constraint by introducing the Lagrange multiplier  $\lambda$  and minimizing the quantity

$$A = xf(\psi_1) + (1-x)f(\psi_2) - \lambda[x\psi_1 + (1-x)\psi_2 - \psi_h]. \quad (1.17)$$

This yields the equations

$$\begin{aligned} \frac{\partial A}{\partial x} &= f(\psi_1) - f(\psi_2) - \lambda(\psi_1 - \psi_2) = 0, \\ \frac{\partial A}{\partial \psi_1} &= xf'(\psi_1) - \lambda x = 0, \\ \frac{\partial A}{\partial \psi_2} &= (1-x)f'(\psi_2) - \lambda(1-x) = 0, \\ \frac{\partial A}{\partial \lambda} &= x\psi_1 + (1-x)\psi_2 - \psi_h = 0. \end{aligned} \quad (1.18)$$

The first three equations yield

$$\lambda = \frac{f(\psi_1) - f(\psi_2)}{\psi_1 - \psi_2} = f'(\psi_1) = f'(\psi_2), \quad (1.19)$$

which is referred to as Maxwell's double-tangent construction. This is valid for arbitrary functional forms of the Helmholtz free energy.

The specific form for  $f(T, \psi)$  in Equation 1.14 is an even function of  $\psi$  with  $f(T, -\psi) = f(T, \psi)$ . Further,  $f(T, \psi)$  has a single minimum at  $\psi = 0$  for  $T > T_c = qJ$ . Thus, the only solution of the double-tangent construction is  $\psi_1 = \psi_2$ . In that case, the constraint in Equation 1.15 yields  $\psi_1 = \psi_h$ , corresponding to the homogeneous state.

For  $T < T_c$ ,  $f(T, \psi)$  has a symmetric double-well structure with extrema at  $f'(T, \psi_0) = 0$ , that is,

$$\psi_0 = \tanh(\beta qJ\psi_0). \quad (1.20)$$

The states with non-zero  $\psi_0$  correspond to lower free energy than the state with  $\psi_0 = 0$ . Thus, a possible solution to the double-tangent construction is

$$\psi_1 = -\psi_0, \quad \psi_2 = +\psi_0, \quad (1.21)$$

where  $\psi_0$  is the positive solution of Equation 1.20. However, this is only an acceptable solution if the lever rule can be satisfied, that is,  $-\psi_0 < \psi_h < \psi_0$ . Thus, phase separation occurs at  $T < T_c$  only if  $|\psi_h| < \psi_0$ . When phase separation does occur, the segregated states have the composition  $-\psi_0$  (B-rich) and  $+\psi_0$  (A-rich), respectively. The resultant phase diagram in the  $(c_A, T/T_c)$ -plane is shown in Figure 1.3.

The phase diagrams in Figures 1.2 and 1.3 will provide the basis for our subsequent discussion of phase-ordering dynamics.

## 1.3 KINETIC ISING MODELS

### 1.3.1 INTRODUCTION

The above discussion has clarified the utility of Ising-like models in a wide range of problems. We next consider the issue of *kinetics of Ising models*. For simplicity, we restrict our discussion to the spin-1/2 model described by Equation 1.1. The generalization to higher-spin models is straightforward. The Ising spin variables do not have intrinsic dynamics, as is seen by constructing the relevant Poisson bracket. In order to associate kinetics with the Ising model, we assume that it is placed in contact with a heat bath that generates stochastic spin-flips ( $S_i \rightarrow -S_i$ ) in the system [6]. The heat bath can be interpreted as consisting of phonons that induce spin-flips via a spin-lattice coupling. The resultant *kinetic Ising model* is referred to as the spin-flip or Glauber model [8] and is appropriate for describing the nonconserved kinetics of the paramagnetic  $\rightarrow$  ferromagnetic transition. The probability of a jump depends on the configuration of all other spins and the heat-bath temperature, in general.

Next, consider the case where the Ising model describes a lattice gas or a binary (AB) mixture. The appropriate microscopic kinetics involves the diffusion of atoms, for example, atomic jumps to vacant sites in the lattice gas, or  $A \leftrightarrow B$  interchanges in the binary mixture. Thus, the heat bath causes spin-exchanges rather than spin-flips, that is,  $S_i$  jumps from  $+1 \rightarrow -1$  while a neighbor  $S_j$  *simultaneously* jumps from  $-1 \rightarrow +1$ . This process mimics phonon-induced atomic jumps. The resultant model is referred to as the spin-exchange or Kawasaki model [9,10].

It should be emphasized that transition probabilities in both the Glauber and Kawasaki models must satisfy the *detailed-balance condition* [11], which will be discussed shortly. Thus, although the two models describe different time-dependent behavior, the equilibrium state is *unique*. As  $t \rightarrow \infty$ , we recover properties calculable from the *equilibrium* statistical mechanics of the Ising model in an appropriate ensemble.

### 1.3.2 THE SPIN-FLIP GLAUBER MODEL

In the Glauber model, the heat bath induces fluctuations in the system in the form of single-spin-flip processes [8]. The Glauber model describes nonconserved kinetics because the spin-flip processes make the total magnetization  $M = \sum_{i=1}^N S_i$  time-dependent. Let us examine the evolution of the probability distribution for the spin configuration  $\{S_i\}$  of a system with  $N$  spins. In this context, we introduce the conditional probability  $P(\{S_i^0\}, 0 | \{S_i\}, t)$ , which is the probability that the  $i$ th spin is in state  $S_i$  ( $i = 1 \rightarrow N$ ) at time  $t$ , given that it was in state  $S_i^0$  ( $i = 1 \rightarrow N$ ) at time  $t = 0$ . The evolution of  $P$  is described by the master equation [11]:

$$\begin{aligned} \frac{d}{dt}P(\{S_i\}, t) = & - \sum_{j=1}^N W(S_1, \dots, S_j, \dots, S_N | S_1, \dots, -S_j, \dots, S_N) P(\{S_i\}, t) \\ & + \sum_{j=1}^N W(S_1, \dots, -S_j, \dots, S_N | S_1, \dots, S_j, \dots, S_N) P(\{S'_i\}, t), \end{aligned} \quad (1.22)$$

where we suppress the argument  $(\{S_i^0\}, 0)$ , for compactness. The first term on the RHS of Equation 1.22 corresponds to the *loss of probability* for the state  $\{S_i\}$  due to the spin-flip  $S_j \rightarrow -S_j$ . The second term on the RHS denotes the *gain of probability* for the state  $\{S_i\}$  due to a spin-flip  $S'_j \rightarrow -S'_j$  in a state  $\{S'_i\}$  with

$$\begin{aligned} S'_i &= S_i \quad \text{for } i \neq j, \\ S'_j &= -S_j. \end{aligned} \quad (1.23)$$

Equation 1.22 assumes that the underlying stochastic process is Markovian. The essential physical input is provided by the modeling of the *transition matrix*  $W(\{S_i\} | \{S'_i\})$  for the change  $\{S_i\}$  to  $\{S'_i\}$ . The choice of  $W$  must be such that the

ensemble approaches the equilibrium distribution  $P_{\text{eq}}(\{S_i\})$  as  $t \rightarrow \infty$ :

$$P_{\text{eq}}(\{S_i\}) = \frac{1}{Z(T, h, N)} \exp[-\beta(H - hM)]. \quad (1.24)$$

Here,  $Z$  is the partition function, which is defined as

$$Z(T, h, N) = \sum_{\{S_i\}} \exp[-\beta(H - hM)]. \quad (1.25)$$

To ensure this, the transition probability  $W(\{S_i\}|\{S'_i\})$  should obey the *detailed-balance condition* [11]:

$$W(\{S_i\}|\{S'_i\})P_{\text{eq}}(\{S_i\}) = W(\{S'_i\}|\{S_i\})P_{\text{eq}}(\{S'_i\}). \quad (1.26)$$

Clearly, in the equilibrium ensemble, this guarantees that the number of systems making the transition from  $\{S_i\} \rightarrow \{S'_i\}$  is balanced by the number of systems making the reverse transition  $\{S'_i\} \rightarrow \{S_i\}$ . Thus, the probability distribution  $P_{\text{eq}}$  is independent of time, as expected. Further, an arbitrary distribution  $P(\{S_i\}, t) \rightarrow P_{\text{eq}}(\{S_i\})$  as  $t \rightarrow \infty$  under Equation 1.22, provided that  $W$  obeys the detailed-balance condition. For the proof of this, we refer the reader to the book by Van Kampen [11].

It is evident that there are many choices of  $W$  that satisfy the condition in Equation 1.26. We choose the Suzuki–Kubo form [12]:

$$W(\{S_i\}|\{S'_i\}) = \frac{\lambda}{2} \left\{ 1 - \tanh \left[ \frac{\beta \Delta(H - hM)}{2} \right] \right\}, \quad (1.27)$$

where  $\lambda^{-1}$  sets the timescale of the nonequilibrium process. Here,  $\Delta(H - hM)$  denotes the enthalpy difference between the final state  $\{S'_i\}$  and the initial state  $\{S_i\}$ . It is straightforward to confirm that this form of  $W$  satisfies the detailed-balance condition.

For the spin-flip Ising model, the states  $\{S'_i\}$  and  $\{S_i\}$  differ only in one spin, that is,  $S'_j = -S_j$ . Then

$$\begin{aligned} (H - hM)_{\text{initial}} &= -JS_j \sum_{L_j} S_{L_j} - hS_j + \text{other terms}, \\ (H - hM)_{\text{final}} &= JS_j \sum_{L_j} S_{L_j} + hS_j + \text{other terms}, \end{aligned} \quad (1.28)$$

where  $L_j$  denotes the nearest neighbors (nn) of  $j$ . Thus

$$\Delta(H - hM) = 2JS_j \sum_{L_j} S_{L_j} + 2hS_j, \quad (1.29)$$



and

$$\begin{aligned} W(\{S_i\}|\{S'_i\}) &= \frac{\lambda}{2} \left[ 1 - \tanh \left( \beta J S_j \sum_{L_j} S_{L_j} + \beta h S_j \right) \right] \\ &= \frac{\lambda}{2} \left[ 1 - S_j \tanh \left( \beta J \sum_{L_j} S_{L_j} + \beta h \right) \right]. \end{aligned} \quad (1.30)$$

In Equation 1.30, we can bring  $S_j$  outside the argument of the tanh-function because it only takes the values  $+1$  or  $-1$ . We replace the form of  $W$  from Equation 1.30 in Equation 1.22 to obtain the explicit form of the master equation:

$$\begin{aligned} \frac{d}{dt} P(\{S_i\}, t) &= -\frac{\lambda}{2} \sum_{j=1}^N \left[ 1 - S_j \tanh \left( \beta J \sum_{L_j} S_{L_j} + \beta h \right) \right] P(\{S_i\}, t) \\ &\quad + \frac{\lambda}{2} \sum_{j=1}^N \left[ 1 + S_j \tanh \left( \beta J \sum_{L_j} S_{L_j} + \beta h \right) \right] P(\{S'_i\}, t). \end{aligned} \quad (1.31)$$

We can use this master equation to obtain the evolution of the magnetization:

$$\langle S_k \rangle = \sum_{\{S_i\}} S_k P(\{S_i\}, t). \quad (1.32)$$

We multiply both sides of Equation 1.31 by  $S_k$  and sum over all configurations to obtain

$$\begin{aligned} \frac{d}{dt} \langle S_k \rangle &= -\frac{\lambda}{2} \sum_{j=1}^N \sum_{\{S_i\}} S_k \left[ 1 - S_j \tanh \left( \beta J \sum_{L_j} S_{L_j} + \beta h \right) \right] P(\{S_i\}, t) \\ &\quad + \frac{\lambda}{2} \sum_{j=1}^N \sum_{\{S_i\}} S_k \left[ 1 + S_j \tanh \left( \beta J \sum_{L_j} S_{L_j} + \beta h \right) \right] P(\{S'_i\}, t) \\ &\equiv A + B. \end{aligned} \quad (1.33)$$

In the second term on the RHS of Equation 1.33, we redefine  $S_j = -\bar{S}_j$ . Clearly, the sum  $\sum_{S_j=\pm 1}$  is equivalent to the sum  $\sum_{\bar{S}_j=\pm 1}$ . Therefore, the terms in  $A$  and  $B$  cancel

with each other, except for the case  $j = k$ . This yields the following evolution equation for the magnetization:

$$\begin{aligned} \lambda^{-1} \frac{d}{dt} \langle S_k \rangle &= - \sum_{\{S_i\}} S_k \left[ 1 - S_k \tanh \left( \beta J \sum_{L_k} S_{L_k} + \beta h \right) \right] P(\{S_i\}, t) \\ &= - \langle S_k \rangle + \left\langle \tanh \left( \beta J \sum_{L_k} S_{L_k} + \beta h \right) \right\rangle, \end{aligned} \quad (1.34)$$

where we have used  $S_k^2 = 1$ .

### 1.3.2.1 Mean-Field Approximation

Unfortunately, the exact time-dependent Equation 1.34 is analytically intractable in  $d \geq 2$ . (For the  $d = 1$  solution, see the work of Glauber [8].) The main obstacle is that the second term on the RHS of Equation 1.34 yields a set of higher-order correlation functions, as can be seen by expanding the tanh-function. These dynamical equations can be rendered tractable by invoking the MF approximation, which truncates the hierarchy by neglecting correlations between different sites, that is, the average of the product of spin operators is replaced by the product of their averages. The result of such a random-phase decoupling is that the angular brackets denoting the statistical average can be taken inside the argument of the tanh-function [13, 14]. Thus, we obtain

$$\lambda^{-1} \frac{d}{dt} \langle S_k \rangle = - \langle S_k \rangle + \tanh \left( \beta J \sum_{L_k} \langle S_{L_k} \rangle + \beta h \right). \quad (1.35)$$

For time-independent effects in equilibrium, the LHS of Equation 1.35 is identically zero. Thus, we have (as  $t \rightarrow \infty$ )

$$\langle S_k \rangle^{\text{eq}} = \tanh \left( \beta J \sum_{L_k} \langle S_{L_k} \rangle^{\text{eq}} + \beta h \right). \quad (1.36)$$

Notice that Equation 1.35 is nonlinear because of the presence of the tanh-function and is only tractable numerically. These equations are often referred to as *mean-field dynamical models* in the literature [15–19]. A further simplification can be effected by expanding the tanh-function and retaining only leading terms. For simplicity, we consider the case of zero magnetic field, that is,  $h = 0$ . We can then expand various

terms on the RHS of Equation 1.35 as follows:

$$\sum_{L_k} \langle S_{L_k} \rangle \simeq q\psi(\vec{r}_k, t) + a^2 \nabla_k^2 \psi(\vec{r}_k, t) + \text{higher-order terms}, \quad (1.37)$$

where  $a$  is the lattice spacing. Further,

$$\begin{aligned} \tanh \left( \beta J \sum_{L_k} \langle S_{L_k} \rangle \right) &\simeq \beta J \sum_{L_k} \langle S_{L_k} \rangle - \frac{1}{3} \left( \beta J \sum_{L_k} \langle S_{L_k} \rangle \right)^3 + \text{higher-order terms} \\ &\simeq \frac{T_c}{T} \psi(\vec{r}_k, t) - \frac{1}{3} \left( \frac{T_c}{T} \right)^3 \psi(\vec{r}_k, t)^3 + \frac{T_c}{qT} a^2 \nabla_k^2 \psi(\vec{r}_k, t) \\ &\quad + \text{other terms}, \end{aligned} \quad (1.38)$$

where we have used Equation 1.37 to obtain the second expression. Therefore, the order-parameter equation for the Glauber–Ising model simplifies as

$$\lambda^{-1} \frac{\partial}{\partial t} \psi(\vec{r}, t) = \left( \frac{T_c}{T} - 1 \right) \psi - \frac{1}{3} \left( \frac{T_c}{T} \right)^3 \psi^3 + \frac{T_c}{qT} a^2 \nabla^2 \psi + \text{other terms}, \quad (1.39)$$

where we have dropped the subscript  $k$  for the position variable.

At this stage, a few remarks are in order. Firstly, Equation 1.39 is referred to as the *time-dependent Ginzburg–Landau* (TDGL) equation. We will discuss the general formulation of the TDGL equation in Section 1.4.1. Secondly, the approximation of neglecting the higher-order terms in Equation 1.39 is justifiable only for  $T \simeq T_c$ , where the order parameter is small. However, it is generally believed that the TDGL equation is valid even for deep quenches ( $T \ll T_c$ ), at least in terms of containing the correct physics.

### 1.3.3 THE SPIN-EXCHANGE KAWASAKI MODEL

We mentioned earlier that the Glauber model, which assumes single-spin-flip processes, is appropriate for nonconserved kinetics. On the other hand, when the Ising model describes either phase separation ( $J > 0$ ) or order-disorder ( $J < 0$ ) transitions in an AB mixture [1,7,20,21], the Glauber model is not applicable. For a binary mixture, the Ising spin variable models the presence of an A- or B-atom on a lattice site. Thus, the appropriate microscopic dynamics should involve random exchanges of A- and B-atoms at neighboring sites, with their individual numbers being constant. In practice, these jumps are actually mediated by vacancies [22–25], and the system should be described as a ternary (ABV) mixture [18,19,26,27]. However, when the vacancy concentration is small, it is reasonable to ignore vacancies and assume that the underlying stochastic process is a spin-exchange. As stated

earlier, this corresponds to the Kawasaki model, which is based on a stationary Markov process involving a spin-exchange mechanism [9,10]. The resultant master equation is as follows:

$$\begin{aligned} \frac{d}{dt}P(\{S_i\}, t) = & - \sum_{j=1}^N \sum_{k \in L_j} W(S_1, \dots, S_j, S_k, \dots, S_N | S_1, \dots, S_k, S_j, \dots, S_N) P(\{S_i\}, t) \\ & + \sum_{j=1}^N \sum_{k \in L_j} W(S_1, \dots, S_k, S_j, \dots, S_N | S_1, \dots, S_j, S_k, \dots, S_N) P(\{S'_i\}, t). \end{aligned} \quad (1.40)$$

The first term on the RHS is the loss of probability for the state  $\{S_i\}$  due to the spin-exchange  $S_j \leftrightarrow S_k$ . We consider only nearest-neighbor exchanges, where site  $k \in L_j$ , that is, the nearest-neighbors of  $j$ . The second term on the RHS corresponds to the gain of probability for the state  $\{S_i\}$  due to an exchange  $S'_j \leftrightarrow S'_k$  in a state  $\{S'_i\}$ . The state  $\{S'_i\}$  differs from the state  $\{S_i\}$  in only two spins:

$$\begin{aligned} S'_i &= S_i \quad \text{for } i \neq j, k, \\ S'_j &= S_k, \\ S'_k &= S_j. \end{aligned} \quad (1.41)$$

As in the Glauber case, the transition probability  $W(\{S_i\}|\{S'_i\})$  must obey the detailed-balance condition. As we have seen in Section 1.2.2, the binary mixture is described by an ensemble with fixed  $(T, M, N)$ , where the “magnetization”  $M = \sum_{i=1}^N S_i = N_A - N_B$ . The corresponding equilibrium distribution is

$$P_{\text{eq}}(\{S_i\}) = \frac{1}{Z(T, M, N)} \exp(-\beta H) \delta_{\sum_i S_i, M}, \quad (1.42)$$

where the Kronecker delta confines the distribution to configurations with  $\sum_{i=1}^N S_i = M$ . The appropriate partition function is

$$Z(T, M, N) = \sum_{\{S_i\}} \exp(-\beta H) \delta_{\sum_i S_i, M}. \quad (1.43)$$

Again, we choose the Suzuki–Kubo form for the transition probability in Equation 1.40:

$$W(\{S_i\}|\{S'_i\}) = \frac{\lambda}{2} \left[ 1 - \tanh\left(\frac{\beta \Delta H}{2}\right) \right], \quad (1.44)$$

where  $\Delta H$  is the change in energy due to the spin-exchange  $S_j \leftrightarrow S_k$ . For the Ising model,

$$\begin{aligned} H_{\text{initial}} &= -JS_j \sum_{L_j \neq k} S_{L_j} - JS_k \sum_{L_k \neq j} S_{L_k} - JS_j S_k + \text{other terms}, \\ H_{\text{final}} &= -JS_k \sum_{L_j \neq k} S_{L_j} - JS_j \sum_{L_k \neq j} S_{L_k} - JS_j S_k + \text{other terms}. \end{aligned} \quad (1.45)$$

Thus, the energy change resulting from the spin exchange is

$$\Delta H = J(S_j - S_k) \sum_{L_j \neq k} S_{L_j} - J(S_j - S_k) \sum_{L_k \neq j} S_{L_k}, \quad (1.46)$$

and

$$\begin{aligned} W(\{S_i\}|\{S'_i\}) &= \frac{\lambda}{2} \left\{ 1 - \tanh \left[ \frac{\beta J}{2} (S_j - S_k) \sum_{L_j \neq k} S_{L_j} - \frac{\beta J}{2} (S_j - S_k) \sum_{L_k \neq j} S_{L_k} \right] \right\} \\ &= \frac{\lambda}{2} \left\{ 1 - \frac{S_j - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_j \neq k} S_{L_j} - \sum_{L_k \neq j} S_{L_k} \right) \right] \right\}. \end{aligned} \quad (1.47)$$

In Equation 1.47, we have used the fact that  $(S_j - S_k)/2 = 0, \pm 1$  to factor it out of the argument of the tanh-function. Therefore, the master equation has the form

$$\begin{aligned} \frac{d}{dt} P(\{S_i\}, t) &= -\frac{\lambda}{2} \sum_{j=1}^N \sum_{k \in L_j} \left\{ 1 - \frac{S_j - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_j \neq k} S_{L_j} - \sum_{L_k \neq j} S_{L_k} \right) \right] \right\} P(\{S_i\}, t) \\ &\quad + \frac{\lambda}{2} \sum_{j=1}^N \sum_{k \in L_j} \left\{ 1 + \frac{S_j - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_j \neq k} S_{L_j} - \sum_{L_k \neq j} S_{L_k} \right) \right] \right\} P(\{S'_i\}, t). \end{aligned} \quad (1.48)$$

We can obtain an evolution equation for the order parameter by multiplying both sides of Equation 1.48 with  $S_n$  and summing over all configurations:

$$\begin{aligned} \frac{d}{dt} \langle S_n \rangle = & -\frac{\lambda}{2} \sum_{\{S_i\}} \sum_{j=1}^N \sum_{k \in L_j} S_n \left\{ 1 - \frac{S_j - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_j \neq k} S_{L_j} - \sum_{L_k \neq j} S_{L_k} \right) \right] \right\} P(\{S_i\}, t) \\ & + \frac{\lambda}{2} \sum_{\{S_i\}} \sum_{j=1}^N \sum_{k \in L_j} S_n \left\{ 1 + \frac{S_j - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_j \neq k} S_{L_j} - \sum_{L_k \neq j} S_{L_k} \right) \right] \right\} P(\{S'_i\}, t). \end{aligned} \quad (1.49)$$

In the second term on the RHS of Equation 1.49, we redesignate  $S_j = \bar{S}_k$  and  $S_k = \bar{S}_j$ . This leads to a large-scale cancellation between the first and second terms. The only remaining terms are

$$\begin{aligned} \frac{d}{dt} \langle S_n \rangle = & -\frac{\lambda}{2} \sum_{\{S_i\}} \sum_{k \in L_n} S_n \left\{ 1 - \frac{S_n - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_n \neq k} S_{L_n} - \sum_{L_k \neq n} S_{L_k} \right) \right] \right\} P(\{S_i\}, t) \\ & + \frac{\lambda}{2} \sum_{\{S_i\}} \sum_{k \in L_n} S_k \left\{ 1 + \frac{S_k - S_n}{2} \tanh \left[ \beta J \left( \sum_{L_n \neq k} S_{L_n} - \sum_{L_k \neq n} S_{L_k} \right) \right] \right\} P(\{S_i\}, t) \\ = & -\frac{\lambda}{2} \left\langle \sum_{k \in L_n} (S_n - S_k) \left\{ 1 - \frac{S_n - S_k}{2} \tanh \left[ \beta J \left( \sum_{L_n \neq k} S_{L_n} - \sum_{L_k \neq n} S_{L_k} \right) \right] \right\} \right\rangle. \end{aligned} \quad (1.50)$$

Some algebra yields the exact evolution equation

$$\begin{aligned} 2\lambda^{-1} \frac{d}{dt} \langle S_n \rangle = & -q \langle S_n \rangle + \sum_{L_n} \langle S_{L_n} \rangle \\ & + \sum_{k \in L_n} \left\langle (1 - S_n S_k) \tanh \left[ \beta J \left( \sum_{L_n \neq k} S_{L_n} - \sum_{L_k \neq n} S_{L_k} \right) \right] \right\rangle. \end{aligned} \quad (1.51)$$

This equation is analogous to Equation 1.34, obtained in the context of Glauber kinetics.

Although the Kawasaki model is usually associated with conserved kinetics, we should make a clarifying remark. In the context of binary mixtures, a *ferromagnetic*

interaction ( $J > 0$ ) results in phase separation, that is, the equilibrium system consists of domains of A-rich and B-rich phases. The appropriate order parameter is the difference in densities of A and B and is locally conserved by Kawasaki kinetics. The length scale over which the order parameter is conserved increases if we allow *long-ranged* exchanges rather than only *nearest-neighbor* exchanges. In the limit where the spin exchanges are *infinite-ranged*, the Kawasaki model has *global conservation* rather than *local conservation*. In this case, the Kawasaki model is essentially equivalent to the Glauber model [28,29].

It is also of great interest to consider the binary mixture with *antiferromagnetic* interactions,  $J < 0$ . In this case, there is a phase transition from a high-temperature disordered phase to a low-temperature ordered phase, where the A- and B-atoms order on alternate sub lattices. The appropriate order parameter is now the *staggered magnetization*, which is the difference between the two sub lattice *magnetizations*. This quantity is not conserved by Kawasaki kinetics, though the overall concentration is conserved. For the AB alloy with equal fractions of A and B, the antiferromagnetic case with Kawasaki kinetics is equivalent to the ferromagnetic Ising model with Glauber kinetics [30]. For asymmetric compositions, novel features arise due to the conserved concentration variable.

### 1.3.3.1 Mean-Field Approximation

As in the Glauber case, Equation 1.51 is the first of a hierarchy of equations involving higher-order correlations of the spin variable. This hierarchy can be truncated by invoking the MF approximation, that is, by replacing the expectation value of a function of spin variables by the function of the expectation values of the spin variables. The resultant MF dynamical model is

$$\begin{aligned}
 2\lambda^{-1} \frac{d}{dt} \langle S_n \rangle = & -q \langle S_n \rangle + \sum_{L_n} \langle S_{L_n} \rangle \\
 & + \sum_{k \in L_n} (1 - \langle S_n \rangle \langle S_k \rangle) \tanh \left[ \beta J \left( \sum_{L_n} \langle S_{L_n} \rangle - \sum_{L_k} \langle S_{L_k} \rangle \right) \right].
 \end{aligned}
 \tag{1.52}$$

Notice that the restrictions on the summations inside the tanh-function have been dropped in the MF approximation. This is necessary for Equation 1.52 to contain the correct MF solution in Equation 1.36 [13]. Recall the MF solution for the  $h = 0$  case:

$$\langle S_k \rangle^{\text{eq}} = \tanh \left( \beta J \sum_{L_k} \langle S_{L_k} \rangle^{\text{eq}} \right).
 \tag{1.53}$$

If we replace this in the RHS of Equation 1.52, we obtain

$$\begin{aligned}
 \text{RHS} &= -q \langle S_n \rangle^{\text{eq}} + \sum_{L_n} \langle S_{L_n} \rangle^{\text{eq}} + \sum_{k \in L_n} (1 - \langle S_n \rangle^{\text{eq}} \langle S_k \rangle^{\text{eq}}) \\
 &\quad \times \left[ \frac{\tanh(\beta J \sum_{L_n} \langle S_{L_n} \rangle^{\text{eq}}) - \tanh(\beta J \sum_{L_k} \langle S_{L_k} \rangle^{\text{eq}})}{1 - \tanh(\beta J \sum_{L_n} \langle S_{L_n} \rangle^{\text{eq}}) \tanh(\beta J \sum_{L_k} \langle S_{L_k} \rangle^{\text{eq}})} \right] \\
 &= -q \langle S_n \rangle^{\text{eq}} + \sum_{L_n} \langle S_{L_n} \rangle^{\text{eq}} + \sum_{L_n} (\langle S_n \rangle^{\text{eq}} - \langle S_{L_n} \rangle^{\text{eq}}) \\
 &= 0,
 \end{aligned} \tag{1.54}$$

as expected.

Finally, let us derive a partial differential equation for the order parameter. This is the conserved counterpart of the TDGL equation we derived for the magnetization in Section 1.3.2. We can simplify the RHS of Equation 1.52 by using the identity

$$\begin{aligned}
 \tanh(X - Y) &= \frac{\tanh X - \tanh Y}{1 - \tanh X \tanh Y}, \quad \text{where} \\
 X &= \beta J \sum_{L_n} \langle S_{L_n} \rangle, \\
 Y &= \beta J \sum_{L_k} \langle S_{L_k} \rangle.
 \end{aligned} \tag{1.55}$$

We are interested in the late-stage dynamics, where the system has equilibrated locally and Equation 1.53 applies. Then, we make the approximation:

$$(1 - \langle S_n \rangle \langle S_k \rangle) \left( \frac{\tanh X - \tanh Y}{1 - \tanh X \tanh Y} \right) \simeq \tanh X - \tanh Y. \tag{1.56}$$

Therefore, we can rewrite Equation 1.52 as

$$\begin{aligned}
 2\lambda^{-1} \frac{d}{dt} \langle S_n \rangle &\simeq \sum_{L_n} (\langle S_{L_n} \rangle - \langle S_n \rangle) \\
 &\quad + \sum_{k \in L_n} \left[ \tanh \left( \beta J \sum_{L_n} \langle S_{L_n} \rangle \right) - \tanh \left( \beta J \sum_{L_k} \langle S_{L_k} \rangle \right) \right] \\
 &= \Delta_D \left[ \langle S_n \rangle - \tanh \left( \beta J \sum_{L_n} \langle S_{L_n} \rangle \right) \right],
 \end{aligned} \tag{1.57}$$



where  $\Delta_D$  denotes the discrete Laplacian operator. We can use the Taylor expansion in Equation 1.38 to obtain the coarse-grained version of Equation 1.57 as

$$2\lambda^{-1} \frac{\partial}{\partial t} \psi(\vec{r}, t) = -a^2 \nabla^2 \left[ \left( \frac{T_c}{T} - 1 \right) \psi - \frac{1}{3} \left( \frac{T_c}{T} \right)^3 \psi^3 + \frac{T_c}{qT} a^2 \nabla^2 \psi \right] + \text{other terms}, \quad (1.58)$$

where  $a$  is the lattice spacing.

Equation 1.58 is known as the Cahn–Hilliard (CH) equation and is the standard model for phase separation driven by diffusion. In Section 1.5.1, we will derive the CH equation using phenomenological arguments.

## 1.4 DOMAIN GROWTH IN SYSTEMS WITH NONCONSERVED KINETICS

### 1.4.1 CASE WITH SCALAR ORDER PARAMETER

In Figure 1.2, we had shown the phase diagram for a ferromagnet. The corresponding ordering problem considers a paramagnetic system at  $T > T_c, h = 0$  for time  $t < 0$ . At  $t = 0$ , the system is rapidly quenched to  $T < T_c$ , where the preferred equilibrium state is spontaneously magnetized. The *far-from-equilibrium* disordered system evolves toward its new equilibrium state by separating into domains that are rich in either up or down spins (see Figure 1.4). These domains coarsen with time and are characterized by a growing length scale  $L(t)$ . A finite system becomes ordered in either of the two equivalent states (up or down) as  $t \rightarrow \infty$ .

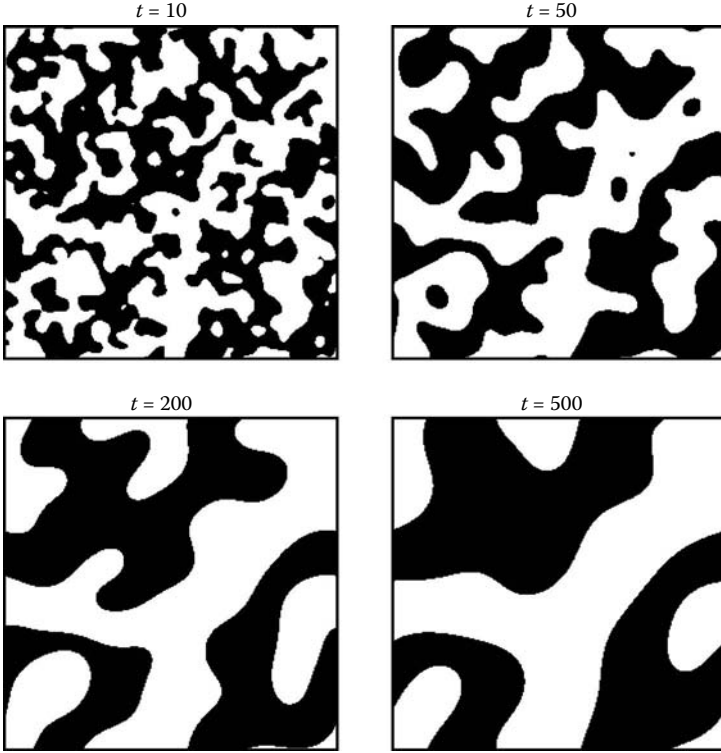
At the microscopic level, this evolution can be described by an Ising model with Glauber spin-flip kinetics, as discussed in Section 1.3.2. At the coarse-grained level, the appropriate order parameter to describe the system is the local magnetization  $\psi(\vec{r}, t)$ . In Section 1.3.2, we had used the Glauber–Ising model to derive the TDGL equation 1.39, which governs the evolution of the order parameter. More generally, the TDGL equation models the dissipative (over-damped) relaxation of a ferromagnetic system to its free-energy minimum:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = -\Gamma \frac{\delta G[\psi]}{\delta \psi} + \theta(\vec{r}, t). \quad (1.59)$$

In Equation 1.59,  $\Gamma$  denotes the inverse damping coefficient; and  $\delta G/\delta \psi$  is the functional derivative of the free-energy functional:

$$G[\psi] = \int d\vec{r} \left[ g(\psi) + \frac{1}{2} K (\vec{\nabla} \psi)^2 \right]. \quad (1.60)$$

Typical forms of the local free energy  $g(\psi)$  are given in Equations 1.8 and 1.9. The second term on the RHS of Equation 1.60 accounts for surface tension due to inhomogeneities in the order parameter. The parameter  $K (>0)$  measures the strength of the surface tension.



**FIGURE 1.4** Evolution of a disordered ferromagnet, which is quenched to  $T < T_c$  at time  $t = 0$ . These pictures were obtained from a Euler-discretized version of the dimensionless TDGL equation 1.66 with  $h = 0$  and no thermal fluctuations ( $\epsilon = 0$ ). The discretization mesh sizes were  $\Delta t = 0.1$  and  $\Delta x = 1$  in time and space, respectively. The initial condition  $\psi(\vec{r}, 0)$  consisted of small-amplitude fluctuations about  $\psi = 0$ . The lattice size was  $256^2$ , and periodic boundary conditions were applied in both directions. Regions with up spins ( $\psi > 0$ ) and down spins ( $\psi < 0$ ) are marked black and white, respectively.

The noise term in Equation 1.59 is also space- and time-dependent and satisfies the fluctuation-dissipation relation:

$$\begin{aligned} \overline{\theta(\vec{r}, t)} &= 0, \\ \overline{\theta(\vec{r}', t')\theta(\vec{r}'', t'')} &= 2\Gamma k_B T \delta(\vec{r}' - \vec{r}'')\delta(t' - t''), \end{aligned} \quad (1.61)$$

where the bars denote an average over the Gaussian noise ensemble. The presence of the noise term ensures that the system equilibrates to the correct Boltzmann distribution at temperature  $T$ . Equations 1.59 through 1.61 are also referred to as *Model A* of order-parameter kinetics, as discussed by Hohenberg and Halperin [31] in the context of dynamic critical phenomena.

Recall the TDGL equation 1.39, which was derived in Section 1.3.2. We identify it as the deterministic version of the general form in Equation 1.59. Further, the damping coefficient  $\Gamma = \beta\lambda$ , where  $\lambda$  is the inverse timescale of Glauber spin-flips. Finally, the form of the free-energy functional that gives rise to Equation 1.39 is

$$\beta G[\psi] = \int d\vec{r} \left[ -\frac{1}{2} \left( \frac{T_c}{T} - 1 \right) \psi^2 + \frac{1}{12} \left( \frac{T_c}{T} \right)^3 \psi^4 + \frac{T_c}{2qT} a^2 (\vec{\nabla} \psi)^2 \right]. \quad (1.62)$$

For our subsequent discussion, it is convenient to use the general form of the  $\psi^4$ -free energy:

$$G[\psi] = \int d\vec{r} \left[ -\frac{a(T_c - T)}{2} \psi^2 + \frac{b}{4} \psi^4 - h\psi + \frac{K}{2} (\vec{\nabla} \psi)^2 \right], \quad (1.63)$$

where we have introduced the parameters  $a, b > 0$  and a term proportional to the magnetic field; and neglected terms of  $O(\psi^6)$  and higher. The parameters  $a, b$  can be identified by a comparison with the explicit form of the free energy in (say) Equation 1.62. However, it is more appropriate to think of them as phenomenological parameters, without any reference to an underlying microscopic model.

For the  $\psi^4$ -free energy in Equation 1.63, the TDGL equation 1.59 has the form:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = \Gamma \left[ a(T_c - T) \psi - b\psi^3 + h + K \nabla^2 \psi \right] + \theta(\vec{r}, t). \quad (1.64)$$

The parameters in Equation 1.64 can be absorbed into the definitions of space and time by introducing the rescaled variables (for  $T < T_c$ )

$$\begin{aligned} \psi' &= \frac{\psi}{\psi_0}, \quad \psi_0 = \sqrt{\frac{a(T_c - T)}{b}}, \\ t' &= a(T_c - T) \Gamma t, \\ \vec{r}' &= \sqrt{\frac{a(T_c - T)}{K}} \vec{r}, \quad \xi_b = \sqrt{\frac{2K}{a(T_c - T)}}, \\ h' &= \frac{h}{a(T_c - T) \psi_0}, \\ \theta' &= \frac{\theta}{a(T_c - T) \Gamma \psi_0}. \end{aligned} \quad (1.65)$$

Dropping primes, we obtain the dimensionless TDGL equation:

$$\frac{\partial}{\partial t} \psi(\vec{r}, t) = \psi - \psi^3 + h + \nabla^2 \psi + \theta(\vec{r}, t), \quad (1.66)$$

where

$$\begin{aligned}\overline{\theta(\vec{r}, t)} &= 0, \\ \overline{\theta(\vec{r}', t')\theta(\vec{r}'', t'')} &= 2\epsilon\delta(\vec{r}' - \vec{r}'')\delta(t' - t''), \\ \epsilon &= \frac{k_B T b [a(T_c - T)]^{(d-4)/2}}{K^{d/2}}.\end{aligned}\quad (1.67)$$

We will focus on the case with  $h = 0$  (shown in Figure 1.4), where the system evolves into two competing states. There is a *domain boundary* or *interface* that separates regions enriched in the two states. Our analytical understanding of domain growth problems is based on the dynamics of these interfaces.

#### 1.4.1.1 Static Interfaces or Kinks

Consider the deterministic version of the TDGL equation with  $h = 0$ :

$$\frac{\partial}{\partial t}\psi(\vec{r}, t) = \psi - \psi^3 + \nabla^2\psi, \quad (1.68)$$

where we have set  $\epsilon = 0$  in Equation 1.66. The static solution of this equation corresponds to a uniform state with  $\psi_0 = +1$  or  $\psi_0 = -1$ . Another static solution (with higher energy than that of the uniform state) is the *interface* or *kink*, which is obtained as the solution of

$$\frac{d^2\psi_s}{dz^2} + \psi_s - \psi_s^3 = 0. \quad (1.69)$$

The kink solution is

$$\psi_s(z) = \tanh\left[\pm \frac{(z - z_0)}{\sqrt{2}}\right], \quad (1.70)$$

where  $z_0$  (the center of the kink) is arbitrary. The solutions with a positive sign (kink) and negative sign (anti-kink) are shown in Figure 1.5. The kink (anti-kink) goes from  $\psi = -1$  ( $\psi = +1$ ) at  $z = -\infty$  to  $\psi = +1$  ( $\psi = -1$ ) at  $z = \infty$ . The solution differs from  $\psi \simeq \pm 1$  in a small interfacial region only, whose width defines the correlation length  $\xi_b = \sqrt{2}$  (in dimensionless units).

The free energy associated with a configuration  $\psi(\vec{r})$  is (in dimensionless units)

$$G[\psi] = \int d\vec{r} \left[ -\frac{\psi^2}{2} + \frac{\psi^4}{4} + \frac{1}{2}(\vec{\nabla}\psi)^2 \right]. \quad (1.71)$$

Therefore, the free-energy difference between the kink solution and the homogeneous solution  $\psi = \psi_0$  is

$$\Delta G = A \int_{-\infty}^{\infty} dz \left[ -\frac{1}{2}(\psi_s^2 - \psi_0^2) + \frac{1}{4}(\psi_s^4 - \psi_0^4) + \frac{1}{2}\left(\frac{d\psi_s}{dz}\right)^2 \right], \quad (1.72)$$