KINETICS of PHASE TRANSITIONS

Edited by
Sanjay Puri and
Vinod Wadhawan

CRC Press
Taylor & Francis Group

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CRC Press
Taylor & Francis Group
Boca Raton London New York

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CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Printed in the United States of America on acid-free paper
10 9 8 7 6 5 4 3 2 1

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

Library of Congress Cataloging-in-Publication Data

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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http://www.crcpress.com

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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.

Sanjay Puri
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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.

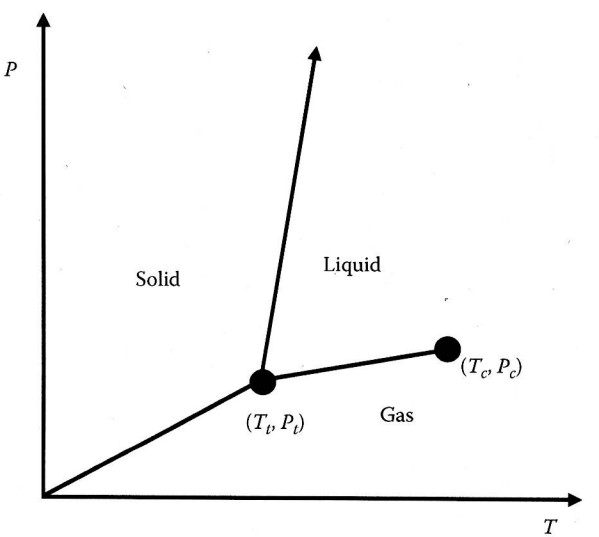

FIGURE 1.1 Phase diagram of a fluid in the (T, P)-plane. The system can exist in either of three phases—liquid, gas, or solid. The solid lines denote lines of first-order phase transitions. At the triple point (T_t, P_t), all three phases coexist. The point labeled (T_c, P_c) is the critical point of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

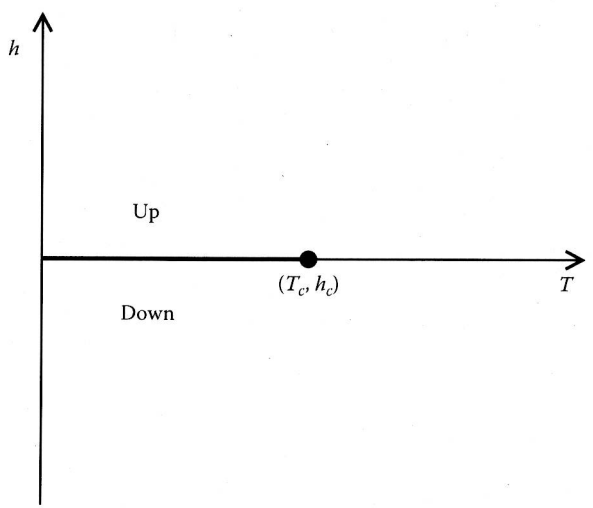

FIGURE 1.2 Phase diagram of a ferromagnet. The system parameters are the temperature (T) and the magnetic field (h). The point ($T_c, h_c = 0$) is a second-order critical point. The line ($T < T_c, h = 0$) corresponds to a line of first-order transitions. At low temperatures ($T < T_c$), the system can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

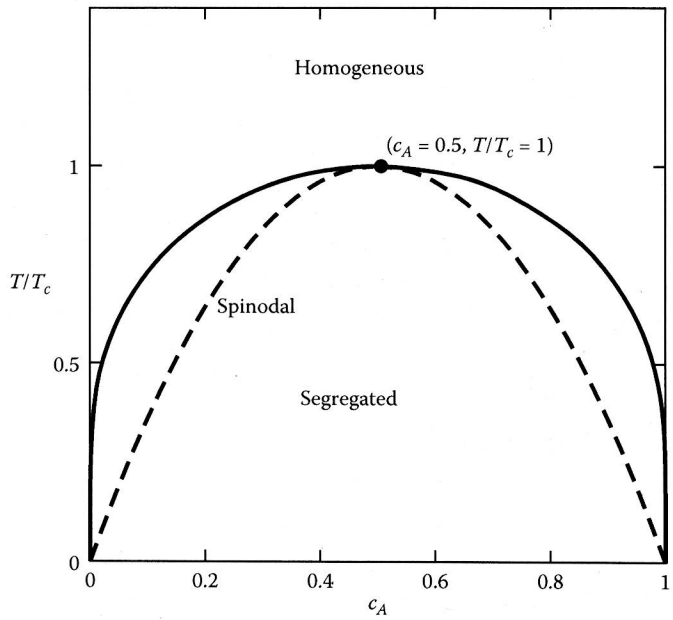

FIGURE 1.3 Phase diagram of a binary (AB) mixture. The system parameters are the concentration of A ($c_A = 1 - c_B$) and the temperature (T). The point ($c_A = 0.5, T/T_c = 1$) corresponds to a second-order critical point. Above the coexistence curve (solid line), the system is in a homogeneous or disordered 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:

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

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 α (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 α and β, located at neighboring sites i and j, respectively. The corresponding Hamiltonian is

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

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_α is the

number of α-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

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

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

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

The corresponding probabilities for a site to have up (↑) or down (↓) spins are

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

Therefore, the entropy for a lattice with N sites is

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

where k_B is the Boltzmann constant.

Then, the Gibbs free energy is obtained as

$$G(\psi) = E(\psi) - hM - TS(\psi), \tag{1.7}$$

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

This yields the free energy per spin as

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

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 ψ^4-form:

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

The order parameter ψ 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, ψ refers to the *sublattice magnetization* or *staggered magnetization* [7].

The equilibrium value of ψ 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 [$\beta = (k_BT)^{-1}$]:

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

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, $\psi(T) \to 1$ as $T \to 0$, and $\psi(T) \to 0$ as $T \to T_c^-$. 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 $(=c_AN)$ atoms of species A and N_B $(=c_BN)$ 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

$$F(T,\psi) = E(\psi) - TS(\psi). \tag{1.13}$$

For the BW free energy, we have the expression

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

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 ψ_1 (with fraction x) and ψ_2 [with fraction $(1-x)$]. The quantity x is determined from the lever rule

$$\psi_h = x\psi_1 + (1-x)\psi_2. \tag{1.15}$$

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

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

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

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

This yields the equations

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