KINETICS OF MATERIALS

Robert W. Balluffi **Samuel M. Allen**

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With Editorial Assistance from Rachel A. Kemper

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Cambridge, Massachusetts

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PREFACE

This textbook has evolved from part of the first-year graduate curriculum in the Department of Materials Science and Engineering at the Massachusetts Institute of Technology (MIT). This curriculum includes four required semester-long subjects—"Materials at Equilibrium," "Mechanical Properties of Materials," "Electrical, Optical, and Magnetic Properties of Materials," and "Kinetic Processes in Materials." Together, these subjects introduce the essential building blocks of materials science and engineering at the beginning of graduate work and establish a foundation for more specialized topics.

Because the entire scope of kinetics of materials is far too great for a semester-length class or a textbook of reasonable length, we cover a range of selected topics representing the basic processes which bring about changes in the size, shape, composition, and atomistic structures of materials. The subject matter was selected with the criterion that structure is all-important in determining the properties (and applications) of materials. Topics concerned with fluid flow and kinetics, which are often important in the processing of materials, have not been included and may be found in standard texts such as those by Bird, Stewart, and Lightfoot [1] and Poirier and Geiger [2]. The major topics included in this book are:

I. Motion of atoms and molecules by diffusion

II. Motion of dislocations and interfaces

III. Morphological evolution due to capillary and applied mechanical forces

IV. Phase transformations

The various topics are generally introduced in order of increasing complexity. The text starts with diffusion, a description of the elementary manner in which atoms and molecules move around in solids and liquids. Next, the progressively more complex problems of describing the motion of dislocations and interfaces are addressed. Finally, treatments of still more complex kinetic phenomena—such as morphological evolution and phase transformations—are given, based to a large extent on topics treated in the earlier parts of the text.

The diffusional transport essential to many of these phenomena is driven by a wide variety of forces. The concept of a basic diffusion potential, which encompasses all of these forces, is therefore introduced early on and then used systematically in the analysis of the many kinetic processes that are considered.

We have striven to develop the subject in a systematic manner designed to provide readers with an appreciation of its analytic foundations and, in many cases, the approximations commonly employed in the field. We provide many extensive derivations of important results to help remove any mystery about their origins. Most attention is paid throughout to kinetic phenomena in crystalline materials; this reflects the interests and biases of the authors. However, selected phenomena in noncrystalline materials are also discussed and, in many cases, the principles involved apply across the board. We hope that with the knowledge gained from this book, students will be equipped to tackle topics that we have not addressed. The book therefore fills a significant gap, as no other currently available text covers a similarly wide range of topics.

The prerequisites for effective use of this book are a typical undergraduate knowledge of the structure of materials (including crystal imperfections), vector calculus and differential equations, elementary elasticity theory, and a somewhat deeper knowledge of classical thermodynamics and statistical mechanics. At MIT the latter prerequisite is met by requiring students to take "Materials at Equilibrium" before tackling "Kinetic Processes in Materials." To facilitate acquisition of prerequisites, we have included important background material in abbreviated form in Appendices. We have provided a list of our most frequently used symbols, which we have tried to keep in correspondence with general usage in the field. Also included are many exercises (with solutions) that amplify and extend the text.

Bibliography

1. B.R. Bird, W.E. Stewart, and N. Lightfoot. *Transport Phenomena.* John Wiley & Sons, New York, 2nd edition, 2002.

2. D.R. Poirier and G.H. Geiger. *Transport Phenomena in Materials Processing.* The Minerals, Metals and Materials Society, Warrendale, PA, 1994.

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Scores of students have used draft versions of this book in their study of kinetics and many have provided thoughtful criticism that has been valuable in making improvements.

Particular thanks are due Catherine M. Bishop, Valerie LeBlanc, Nicolas Mounet, Gilbert Nessim, Nathaniel J. Quitoriano, Joel C. Williams, and Yi Zhang for their careful reading and suggestions. Ellen J. Siem provided illustrations from her Surface Evolver calculations. Scanning electron microscopy expertise was contributed by Jorge Feuchtwanger. Professors Alex King and Hans-Eckart Exner and Dr. Markus Döblinger furnished unpublished micrographs. Angela M. Locknar expended considerable effort securing hard-to-locate bibliographic sources. Andrew Standeven's care in drafting the bulk of the illustrations is appreciated. Jenna Picceri's and Geraldine Sarno's proofreading skills and work on gathering permissions are gratefully acknowledged. Finally, we wish to thank our editor, Rachel A. Kemper, for her invaluable assistance at all stages of the preparation of this work.

We are fortunate to have so many friends and colleagues who donated their time to help us correct and clarify the text. Although we have striven to remove them all, the remaining errors are the responsibility of the authors.

This textbook has evolved over eight years, during which our extended families have provided support, patience, indulgence, and sympathy. We thank you with all of our hearts.

NOTATION

Notation	Definition
$\vec{a}$	Vector a, the column vector $\vec{a}$
$\hat{a}$	Unit vector a
$\underline{A}$, $[A_{ij}]$	Matrix A, matrix A in component form
$\boldsymbol{A}$	Tensor A of rank two or greater
$\vec{a} \cdot \vec{b}$	Scalar, inner or dot product of $\vec{a}$ and $\vec{b}$
$\vec{a} \times \vec{b}$	Vector, outer or cross product of $\vec{a}$ and $\vec{b}$
$\vec{a}^T$, $\underline{A}^T$	Transpose of $\vec{a}$ or $\underline{A}$
$\mathcal{A}, A, a$	Total amount of A, amount of A per mole or per atom as deduced from context, density of A
$\langle a \rangle$	Average value of a
∇a	Gradient of scalar field a
$\nabla \cdot \vec{A}$	Divergence of vector field $\vec{A}$
$\nabla \cdot \nabla a \equiv \nabla^2 a$	Laplacian of scalar field a
δ_{ij}	Kronecker delta, $\delta_{ij} = 1$ for $i = j$; $\delta_{ij} = 0$ if $i \neq j$
$\mathcal{L}\{a\}$ or $\hat{a}$	Laplace transform of a
$\mathrm{Ca}_{\mathrm{K}}^{\bullet}$	Kröger–Vink notation for Ca on K-site with positive effective charge
$\mathrm{V}'_{\mathrm{Ag}}$	Kröger–Vink notation for vacancy on Ag-site with negative effective charge
$\mathrm{S}_{\mathrm{O}}^{\times}$	Kröger–Vink notation for S on O-site with zero effective charge

SYMBOLS—ROMAN

Symbol	Definition	Units
A	Area	m^2
a, b, c	Lattice constants	m
$\vec{b}$, b	Burgers vector, magnitude of Burgers vector	m
$\vec{b}$	Specific magnetic moment	$A\,m^{-1}$
c, c_i	Concentration of molecules or atoms, concentration of species i	m^{-3}, $d = 3$ m^{-2}, $d = 2$ m^{-1}, $d = 1$
D, $\boldsymbol{D}$	Mass diffusivity, diffusivity tensor	$m^2\,s^{-1}$
D^{XL}	Bulk diffusivity in crystalline material free of line or planar imperfections	$m^2\,s^{-1}$
D^B	Boundary diffusivity	$m^2\,s^{-1}$
D^D	Dislocation diffusivity	$m^2\,s^{-1}$
D^L	Liquid diffusivity	$m^2\,s^{-1}$
D^S	Surface diffusivity	$m^2\,s^{-1}$
$\widetilde{D}$	Chemical interdiffusivity	$m^2\,s^{-1}$
$^*D$	Self-diffusivity in pure material	$m^2\,s^{-1}$
$^*D_i$	Self-diffusivity of component i in multicomponent system	$m^2\,s^{-1}$
D_i	Intrinsic diffusivity of component i in multicomponent system	$m^2\,s^{-1}$
d	Spatial dimensionality	–
E	Activation energy	$J\ atom^{-1}$
E	Young's elastic modulus	$Pa = J\,m^{-3}$
$\vec{E}$	Electric field vector	$V\,m^{-1}$
f	Correlation factor for atomic jumps in diffusion	—

SYMBOLS—ROMAN

Symbol	Definition	Units
$\mathcal{F}$, F, f	Helmholtz energy, Helmholtz energy per mole (or particle), Helmholtz energy density	J, $\mathrm{J\,mol^{-1}}$, $\mathrm{J\,m^{-3}}$
$\vec{F}$, $\vec{f}$	Force, force per unit length	N, $\mathrm{N\,m^{-1}}$
$\mathcal{G}$, G, g	Gibbs energy, Gibbs energy per mole (or particle), Gibbs energy density	J, $\mathrm{J\,mol^{-1}}$, $\mathrm{J\,m^{-3}}$
$\mathcal{H}$, H, h	Enthalpy, enthalpy per mole (or particle), enthalpy density	J, $\mathrm{J\,mol^{-1}}$, $\mathrm{J\,m^{-3}}$
h	Planck constant	6.626×10^{-34} J s
I_q, I_i	Current of electrical charge, current of species i	$\mathrm{C\,s^{-1}}$, $\mathrm{s^{-1}}$
$\hat{\imath}, \hat{\jmath}, \hat{k}$	Unit vectors parallel to Cartesian coordinates x, y, z	—
$\vec{J}$, $\vec{J}_i$	Flux, flux of species i	$\mathrm{m^{-2}\,s^{-1}}$
J	Nucleation rate	$\mathrm{m^{-3}\,s^{-1}}$
K	Thermal conductivity	$\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$
K	Rate constant	various
k	Boltzmann constant	$1.38 \times 10^{-23}\mathrm{J\,K^{-1}}$
$L_{\alpha\beta}$	Onsager coupling coefficient (or tensor)	$\mathrm{m^{-2}\,s^{-1}\,N^{-1}}$
M, $\boldsymbol{M}$	Mobility, mobility tensor	various
M_i°	Atomic or molecular weight of species i	$\mathrm{kg\,N_\circ^{-1}}$
m	Mass	kg
N	Number	—
$\mathcal{N}$	Total number of atoms or molecules in subsystem	—
N_c	Number of components in a solution	—
$N_\circ$	Avogadro's number	6.023×10^{23}

SYMBOLS—ROMAN

Symbol	Definition	Units
n	Number per unit volume (concentration)	m^{-3}
$\hat{n}$	Unit normal vector at interface	—
n_d	Instantaneous diffusion-source strength	m^{-2}, $d = 3$ m^{-1}, $d = 2$ number, $d = 1$
P	Pressure	$\mathrm{Pa} = \mathrm{J\,m}^{-3}$
p	Probability	—
$\vec{p}$	Momentum	$\mathrm{kg\,m\,s}^{-1}$
Q	Heat	J
q	Electrical charge	C
R	Radius	m
$\vec{r}$	Position vector relative to origin	m
r, θ, z	Cylindrical coordinates	—
r, θ, ϕ	Spherical coordinates	—
$\mathcal{S}$, S, s	Entropy, entropy per mole (or particle), entropy density	$\mathrm{J\,K}^{-1}$, $\mathrm{J\,K}^{-1}\mathrm{mol}^{-1}$, $\mathrm{J\,K}^{-1}\mathrm{m}^{-3}$
T	Absolute temperature	K
T_m	Absolute melting temperature	K
t	Time	s
$\mathcal{U}$, U, u	Internal energy, internal energy per mole (or particle), internal energy density	J, $\mathrm{J\,mol}^{-1}$, $\mathrm{J\,m}^{-3}$
$\vec{u}$	Displacement field	m

SYMBOLS—ROMAN

Symbol	Definition	Units
V	Volume	m^3
$\vec{v}$, v	Velocity, speed	$\mathrm{m\,s}^{-1}$
v	Specific volume	—
W, w	Work, work per unit volume	J
X_i	Composition variable: mole, atomic, or number fraction of component i	—
x, y, z	Cartesian orthogonal coordinates	m
x_1, x_2, x_3	General coordinates	—
z, z_c	Coordination number, effective coordination number for critical nucleus	—
Z	Partition function	—
Z	Zeldovich factor	—

SYMBOLS—GREEK

Symbol	Definition	Units
Γ', Γ	Atomic or molecular jump frequency for a particular jump, total jump frequency	s^{-1}
γ, $\gamma(\hat{n})$	Surface or interfacial tension, work to produce unit interfacial area at constant stress and temperature at orientation $\hat{n}$	$J\,m^{-2}$
γ_i	Activity coefficient of component i	various
δ	Effective thickness of grain boundary or surface layer; diameter of dislocation core	m
η	Diffusion scaling factor, $x/\sqrt{4Dt}$	—
$\hat{\zeta}$	Unit vector tangent to dislocation	—
ε, $\boldsymbol{\varepsilon}$, ε_{ij}	Component of strain, strain tensor, strain tensor in component form	mm^{-1}
κ, κ_1, κ_2	Mean curvature; principal curvatures	m^{-1}
κ_γ	Weighted mean curvature	$J\,m^{-3}$
κ	Thermal diffusivity	$m^2\,s^{-1}$
λ	Wavelength	m
Λ	Elastic-energy shape factor	—
μ	Elastic shear modulus	$Pa = J\,m^{-3}$
μ, μ_i	Chemical potential, chemical potential of species i	J
μ_i^α, μ_i°	Chemical potential of species i in phase α, chemical potential of species i in reference state	J
ν	Frequency	s^{-1}

SYMBOLS—GREEK

Symbol	Definition	Units
ν	Poisson's ratio	—
$\vec{\xi}$	Capillarity vector	$\mathrm{J\,m^{-2}}$
ρ	Density	$\mathrm{kg\,m^{-3}}$
ρ	Electrical conductivity	$\mathrm{C\,V^{-1}m^{-1}\,s^{-1}}$
σ, $\boldsymbol{\sigma}$, σ_{ij}	Stress, stress tensor, component of stress tensor	$\mathrm{Pa} = \mathrm{J\,m^{-3}}$
$\dot{\sigma}$	Rate of entropy production per unit volume	$\mathrm{J\,m^{-3}\,s^{-1}\,K^{-1}}$
τ	Characteristic time	s
Φ_i	Diffusion potential for species i	J
ϕ	Electrical potential	$\mathrm{J\,C^{-1}}$
χ	Site fraction	—
Ω, Ω_i, $\langle\Omega\rangle$	Atomic volume, atomic volume of component i, average atomic volume	$\mathrm{m^3}$
ω	Angular frequency	$\mathrm{s^{-1}}$

CHAPTER 1

INTRODUCTION

Kinetics of Materials is the study of the rates at which various processes occur in materials—knowledge of which is fundamental to materials science and engineering. Many processes are of interest, including changes of size, shape, composition, and structure. In all cases, the system must be out of equilibrium during these processes if they are to occur at a finite rate. Because the departure from equilibrium may be large or small and because the range of phenomena is so broad, the study of kinetics is necessarily complex. This complexity is reduced by introducing approximations such as the assumption of local equilibrium in certain regions of a system, linear kinetics, or mean-field behavior. In much of this book we employ these approximations.

Ultimately, a knowledge of kinetics is valuable because it leads to prediction of the rates of materials processes of practical importance. Analyses of the kinetics of such processes are included here as an alternative to a purely theoretical approach. Some examples of these processes with well-developed kinetic models are the rates of diffusion of a chemical species through a material, conduction of heat during casting, grain growth, vapor deposition, sintering of powders, solidification, and diffusional creep.

The *mechanisms* by which materials change are of prime importance in determining the kinetics. Materials science and engineering emphasizes the role of a material's microstructure. Structure and mechanisms are the yarn from which materials science is woven [1]. Understanding kinetic processes in, for example, crystalline materials relies as much on a thorough familiarity with vacancies, interstitials, grain

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boundaries, and other crystal imperfections as it does on basic mathematics and physics. Extensive discussion of mechanisms is therefore a feature of this book.

We stress rigorous analysis, where possible, and try to build a foundation for understanding kinetics in preparation for concepts and phenomena that fall beyond the scope of this book. Also, in laying a foundation, we have selected basic topics that we feel will be part of the materials science and engineering curriculum for many years, no matter how technical applications of materials change. A comprehensive reading of this book and an effort at solving the exercises should provide the requisite tools for understanding most of the major aspects of kinetic processes in materials.

1.1 THERMODYNAMICS AND KINETICS

In the study of materials science, two broad topics are traditionally distinguished: thermodynamics and kinetics. *Thermodynamics* is the study of equilibrium states in which state variables of a system do not change with time, and *kinetics* is the study of the rates at which systems that are out of equilibrium change under the influence of various forces. The presence of the word *dynamics* in the term *thermodynamics* is therefore misleading but is retained for historical reasons.

In many cases, the study of kinetics concerns itself with the paths and rates adopted by systems approaching equilibrium. Thermodynamics provides invaluable information about the final state of a system, thus providing a basic reference state for any kinetic theory. Kinetic processes in a large system are typically rapid over short length scales, so that equilibrium is nearly satisfied locally; at the same time, longer-length-scale kinetic processes result in a slower approach to global equilibrium. Therefore, much of the machinery of thermodynamics can be applied locally under an assumption of local equilibrium. It is clear, therefore, that the subject of thermodynamics is closely intertwined with kinetics.

1.1.1 Classical Thermodynamics and Constructions of Kinetic Theories

Thermodynamics grew out of studies of systems that exchange energy. Joule and Kelvin established the relationship between work and the flow of heat which resulted in a statement of the first law of thermodynamics. In Clausius's treatise, *The Mechanical Theory of Heat*, the law of energy conservation was supplemented with a second law that defined entropy, a function that can only increase as an isolated system approaches equilibrium [2]. Poincaré coined the term *thermodynamiques* to refer to the new insights that developed from the first and second laws. Development of thermodynamics in the nineteenth century was devoted to practical considerations of work, energy supply, and efficiency of engines. At the end of the nineteenth century, J. Willard Gibbs transformed thermodynamics into the subject of phase stability, chemical equilibrium, and graphical constructions for analyzing equilibrium that is familiar to students of materials science. Gibbs used the first and second laws rigorously, but focused on the medium that stores energy during a work cycle. From Gibbs's careful and rigorous derivations of equilibrium conditions of matter, the modern subjects of chemical and material thermodynamics were born [3]. Modern theories of statistical and continuum thermodynamics—