Phase Transitions in Materials

Second Edition

The new edition of this popular textbook provides a fundamental approach to phase transformations and thermodynamics of materials. Explanations are emphasized at the level of atoms and electrons, and it comprehensively covers the classical topics from classical metallurgy to nanoscience and magnetic phase transitions. The book has three parts, covering the fundamentals of phase transformations, the origins of the Gibbs free energy, and the major phase transformations in materials science. A fourth part on advanced topics is available online. Much of the content from the first edition has been expanded, notably precipitation transformations in solids, heterogeneous nucleation, and energy, entropy, and pressure. Three new chapters have been added to cover interactions within microstructures, surfaces, and solidification. Containing over 170 end-of-chapter problems, it is a valuable companion to graduate students and researchers in materials science, engineering, and applied physics.

Brent Fultz is the Rawn Professor of Materials Science and Applied Physics at the California Institute of Technology. His awards include the 2016 William Hume-Rothery Award of The Minerals, Metals and Materials Society (TMS). He is a fellow of the American Physical Society (APS), TMS, and the Neutron Scattering Society of America (NSSA).

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BRENT FULTZ
California Institute of Technology

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Contents

Preface

Content

This book explains the thermodynamics and kinetics of most of the important phase transitions in materials science. It is a textbook, so the emphasis is on explanations of phenomena rather than a scholarly assessment of their origins. The goal is explanations that are concise, clear, and reasonably complete. The level and detail are appropriate for upper division undergraduate students and graduate students in materials science and materials physics. The book should also be useful for researchers who are not specialists in these fields. The book is organized for approximately sequential coverage in a graduate-level course. The four parts of the book serve different purposes, however, and should be approached differently.

Part I presents topics that all graduate students in materials science must know.[1] After a general overview of phase transitions, temperature–composition phase diagrams are explained from classical thermodynamics and from the statistical mechanics of Ising lattices. Diffusion, equilibration, and nucleation are then covered, and general aspects of diffusion and nucleation are used with T–c phase diagrams to explain the rates of some phase transformations.

Part II addresses the origins of materials thermodynamics and kinetics at the level of atoms and electrons. Electronic and elastic energy are covered at the level needed in some of the later chapters. The physical origins of entropy (a topic that receives scant coverage in other texts) are presented in the context of phase transitions on Ising lattices. Effects of pressure, combined with temperature, are explained with a few concepts of chemical bonding and antibonding. The thermodynamics of real materials typically involves minimizing a free energy with multiple degrees of freedom, and Chapter 9 shows directions beyond one variable. Chapter 10 on kinetics emphasizes atom movements for diffusion in solids, especially features of atom–vacancy interchanges.

Part III is the longest. It describes important phase transformations in materials, with their underlying concepts. Topics include surface phenomena, melting, solidification, nucleation and growth in solids, spinodal decomposition, phase field theory, continuous ordering, martensitic transformations, phenomena in nanomaterials, and phase transitions involving electrons or spins. Many topics from metallurgy and ceramic engineering are

[1] The author asks graduate students to explain some of the key concepts at a blackboard during their Ph.D. candidacy examinations.

covered, although the connection between processing and properties is less emphasized, allowing for a more concise presentation than in traditional texts.

The online Advanced Topics present modern topics that have proved their importance. These chapters are available online at doi:10.7907/05BY-QX43 and can be downloaded at no cost from https://www.library.caltech.edu. The chapters cover low- and high-temperature treatments of the partition function, nonequilibrium states in crystalline alloys, a *k*-space formulation of elastic energy, fluctuations and how they are measured, high-temperature thermodynamics, the renormalization group, scaling theory, and an introduction to quantum phase transitions. The topics are explained at a fundamental level, but unlike Parts I through III, for conciseness there are more omissions of methods and steps.

Many topics in phase transitions and related phenomena are not covered in this text. These include: polymer flow and dynamics including reptation, phase transitions in fluid systems including phenomena near the critical temperature, crystallographic symmetry in displacive transformations, and massive transformations. Also beyond the scope of the book are computational methods that are increasingly important for studies of phase transformations in materials, including: Monte Carlo methods, molecular dynamics methods (classical and quantum), and density functional theory with time or ensemble averages for materials at finite temperatures.

The field of phase transitions is huge, and continues to grow. This text is a snapshot of the field taken from the viewpoint of the author near the year 2020. Impressively, this field continues to offer a rich source of new ideas and results for both fundamental and applied research, and parts of it will look different in a decade or so. I expect, however, that the core will remain the same – the free energy of materials will be at the center, surrounded by issues of kinetics.

Teaching

I use this text in a course for Ph.D. students in both materials science and in applied physics at the California Institute of Technology. The 10-week course is offered in the third academic quarter as part of a one-year sequence. The first two quarters in this sequence cover thermodynamics and statistical mechanics, so the students are already familiar with using a partition function to obtain thermodynamic quantities. Familiarity with some concepts from solid-state physics and chemistry is certainly helpful, but the text develops many of the important concepts as needed.

In the one-quarter course at Caltech, I cover most topics in Parts I and II, moving in sequence through the chapters. Time limitations force a selection of topics from Part III and Advanced Topics. For example, I tend to cover Chapters 12, 16, 18, and parts of 14, 19, 20 (although sometimes these later parts are replaced by an advanced chapter, such as 25). It is unrealistic to cover the entire content of the book in one course, even with a 15-week semester. An instructor will use discretion in selecting topics for the second half of his or her course.

The problems at the end of each chapter were used for weekly student assignments, and this helped to refine their wording and content. The majority of these problems are based on concepts explained in the text, sometimes filling in explanations or extending the analyses. Other problems, less popular with students, develop new concepts not described in the chapter. These problems usually include longer explanations and hints that may be worth reading even without working the problem. None of the problems are intended to be particularly difficult, and some can be answered quickly with one main idea. For homework, I assign five or six of these problems every week during the term. In their reviews of the course, most students reportedly spend 6–8 hours per week outside the classroom completing these problem sets and reading the text. An online solutions manual is available to course instructors whose identity can be verified. Please ask me for further information.

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Brent Fultz

Notation

a	lattice parameter
A	area
$\vec{A}$	vector potential of magnetic field
A-atom	generic chemical element
APDB	antiphase domain boundary
α	coefficient of linear thermal expansion
α	critical exponent for heat capacity
α-phase	generic phase
α-sublattice	a lattice of like atoms within an ordered structure
α_i	root of Bessel function
α^2	electron–phonon coupling factor
$\vec{b}$	Burgers vector of dislocation
b_{A}	coherent neutron scattering length of isotope A
$b(\vec{k})$	Fourier transform of pairwise energy for two concentration waves
B	bulk modulus
$\vec{B}$	magnetic field
B-atom	generic chemical element
$B(\vec{R})$	pairwise energy between atoms
β	coefficient of volume thermal expansion
β	critical exponent for density
β-phase	generic phase
β-sublattice	a lattice of like atoms within an ordered structure
c	chemical composition (atomic fraction)
c_{l}^*	chemical composition of liquid at liquid–solid interface
c_{s}^*	chemical composition of solid at liquid–solid interface
c	speed of sound or light
c_{A}	concentration of A-atoms
c_{A}	weight of atomic wavefunction on atom A in a molecular wavefunction
C_{el}	electronic heat capacity
$C_P(T)$	heat capacity at constant pressure
$C_V(T)$	heat capacity at constant volume
C_{ij}, C_{ijlm}	elastic constant

D	diffusion coefficient
D	deformation potential
D_{h}	thermal (heat) diffusion coefficient
$\vec{D}$	electric polarization
D_0	prefactor for exponential form of diffusion coefficient
$\tilde{D}(c)$	interdiffusion coefficient
$\underline{D}(\vec{k})$, $D_{ij}(\vec{k})$	dynamical matrix, element of
δ	fractional change in volume (of misfitting sphere)
ΔG_{V}	change in Gibbs free energy per unit volume
ΔG^*	activation barrier for nucleation
$\Delta(\vec{r})$	static wave of chemical concentration
e	charge of electron
e_{A}	energy of an A-atom on a crystal site
e_{AB}	energy of a pair (bond) between an A- and a B-atom
e_{R}, e_{W}	energy of two atoms, A and B, on their right or wrong sublattices
$\vec{e}_{\kappa j}(\vec{k})$	polarization for atom of basis index κ in phonon of $\vec{k}$ in branch j
$\mathrm{erf}(z)$	error function
E	energy, thermodynamic energy
$\vec{E}$	electric field
E_{el}	elastic energy
E_{elec}	electrostatic energy
ε	energy, energy of phonon
ϵ	energy, energy of electron
ϵ	fractional difference in T from T_{c}
ϵ_{F}	Fermi energy
ϵ_j, ϵ_{ij}	strain
η	fractional change of lattice parameter with composition
η	order parameter
f	correlation factor
f_α	(atomic) fraction of α-phase
f_j	interaction free energy
$f(c)$	free energy per unit volume
F	Helmholtz free energy
$\mathcal{F}$	force
$F_\xi(c,T)$	free energy for phase ξ with composition c at temperature T
$g(\varepsilon)$	phonon density of states
$\vec{g}$	reciprocal lattice vector
grad(c) or $\overrightarrow{\nabla c}$	gradient (of concentration)
G	Gibbs free energy
$G(\vec{r},t)$	Van Hove space-time correlation function

$\mathcal{G}$	temperature gradient $\mathrm{d}T/\mathrm{d}x$
γ	coefficient for linear electronic heat capacity vs. T
γ	Grüneisen parameter
γ_j	Grüneisen parameter for phonon mode j
γ_{xy}	shear strain
Γ	atomic jump frequency
Γ	point at origin of reciprocal lattice
h	bond integral
$\hbar$	Planck constant divided by 2π
H	Hamiltonian
$\vec{H}$	magnetic field
$\vec{j}$	flux
$J_0(x)$, $J_1(x)$	Bessel functions of zero and first order
J_n	number of clusters per unit time that change from n to $n+1$
J_{ss}	steady-state flux in number space of cluster sizes
J_{hs}, J_{hl}	heat flux in solid and liquid (1D)
$\vec{J}_{\mathrm{A}}$	flux of A-atoms
$J(\vec{r}_1 - \vec{r}_j)$	magnetic exchange energy
k	partitioning ratio $k = c_{\mathrm{s}}/c_{\mathrm{l}}$
$\vec{k}$	wavevector
k_{B}	Boltzmann constant
κ	coefficient for square gradient energy
κ	Ginzburg–Landau parameter
L	latent heat
L	long-range order parameter
$L(\tau E_0/k_{\mathrm{B}}T)$	Langevin function
LHS	left-hand side
λ	wavelength
λ	electron–phonon coupling parameter
m	mass
m	slope of liquidus curve on phase diagram $\mathrm{d}T_{\mathrm{l}}/\mathrm{d}c$
M	mobility
$\vec{M}$	magnetization
$\mathcal{M}$	Mendeleev number
μ	chemical potential
μ	shear modulus
$\vec{\mu}$	magnetic moment

$n(\varepsilon_i, T)$	Planck distribution
N	number (of atoms)
N_{A}^{α}	number of A-atoms on α-sublattice (point variable)
$N_{\mathrm{AB}}^{\alpha\beta}$	number of A–B pairs with A on α and B on β (pair variable)
$N(k)$	number of quantum states with wavevector less than k
$N(t)$	vector of number occupancies of states at time t
$\tilde{\ }$	
ν	frequency
ν	Poisson ratio
ν	critical exponent for correlation length
ω	angular frequency
Ω	number of states accessible to the system
Ω	atomic volume
Ω_j	configurations of a system with energy j
p_i	probability of a state
$\vec{p}$	momentum
p_{A}	partial pressure of vapor of element A
p_{A}^{α}	probability of A-atom on α-sublattice (point variable)
$p_{\mathrm{AB}}^{\alpha\beta}$	probability of A–B pair with A on α and B on β (pair variable)
P	pressure
P_{th}	thermal pressure (from expansion against a bulk modulus)
$\mathcal{P}$	Péclet number
$\Phi(r)$	interatomic, central-force potential
$\Phi_{\mathrm{M}}(r)$, $\Phi_{\mathrm{L\text{-}J}}(r)$	Morse potential, Lennard-Jones potential
Φ_0	quantum of magnetic flux $hc/2e$
Q	compositional wavevector $2\pi/\lambda$
Q	total electrostatic charge
$\vec{Q}$	momentum transfer in scattering
Q	quality factor of damped harmonic oscillator
r_{B}	Bohr radius $r_{\mathrm{B}} = \hbar^2/(m_e e^2)$
r_{WS}	Wigner–Seitz radius
$\vec{r}_l$	position of unit cell
$\vec{r}_k$	basis vector within unit cell
R	number of right atoms on a sublattice of an ordered structure
$R(Q)$	growth rate for compositional wavevector Q
R^*	critical radius for nucleation
$\vec{R}$	position of atom center
$\vec{R}_n$	displacement after n jumps
$\mathcal{R}$	number of atoms in unit cell
RHS	right-hand side

ρ	density, e.g., [atoms cm^{-3}]
$\rho(\epsilon)$	electronic density of states
$\rho(\epsilon_F)$	electronic density of states at the Fermi energy
$\vec{s}_i$	electronic spin at site i
S	entropy
S	overlap integral
S_{conf}	configurational entropy
S_{vib}	vibrational entropy
S_h	harmonic entropy
S_{qh}	entropy contribution from quasiharmonicity
S_{anh}	entropy contribution from anharmonicity
S_{el}	electronic entropy
S_{epi}	entropy contribution from electron–phonon interaction
S_{mag}	magnetic entropy
$S(\vec{Q}, \omega)$	scattering function
σ	surface energy per unit area
σ	electrical conductivity
σ	spin number (± 1)
σ_{gb}	energy per unit area of grain boundary
σ_{ij}	stress
t	time
T	temperature
T_c	critical temperature
T_C	Curie temperature
T_m	melting temperature
T_N	Néel temperature
$T_1, T_2, \ldots$	sequence of temperatures such that $T_2 > T_1$
$\vec{T}$	translation vector of real space lattice
τ	characteristic time (e.g., for diffusion)
$\vec{\tau}$	electrostatic dipole moment
$\theta(\vec{r})$	Heaviside function, 1 in the region, 0 outside
$\theta(\vec{r}, t)$	phase of wavefunction in space and time
Θ_D	Debye temperature
$\vec{u}(x, y, z)$	displacement vector
U	difference in chemical preferences of A- and B-atoms $U = (e_{AA} - e_{BB})/4V$
U	Coulomb energy penalty for placing a second electron on a site in Hubbard model
Υ_j	Grüneisen parameter for energy of electronic state j

$\vec{v}$	velocity
V	interchange energy $V = (e_{AA} + e_{BB} - 2e_{AB})/4$
V	volume
$V(\vec{r})$	potential energy
V_Q	quantum volume, related to cube of de Broglie wavelength
v_0	volume per atom
W	number of wrong atoms on a sublattice of an ordered structure
W_{ij}	transition rate from state j to state i
$W^{\uparrow}_{\beta A \alpha}$	rate of increase of LRO parameter by jump of A from β- to α-sublattice
$\underset{\approx}{W}(\Delta t)$	transition matrix for time interval Δt
ξ	correlation function
ξ	length
$\{\chi_i\}$	reaction coordinates
χ	susceptibility
Y	Young's modulus
$\psi(\vec{r})$	wavefunction
z	coordination number of lattice
z	partition function of subsystem
Z	partition function
$\mathcal{Z}$	Zeldovich factor