Phase Transition Dynamics

Phase transition dynamics is of central importance in current condensed matter physics. Akira Onuki provides a systematic treatment of a wide variety of topics including critical dynamics, phase ordering, defect dynamics, nucleation, and pattern formation by constructing time-dependent Ginzburg–Landau models for various systems in physics, metallurgy, and polymer science.

The book begins with a summary of advanced statistical–mechanical theories including the renormalization group theory applied to spin and fluid systems. Fundamental dynamical theories are then reviewed before the kinetics of phase ordering, spinodal decomposition, and nucleation are covered in depth in the main part of the book. The phase transition dynamics of real systems are discussed, treating interdisciplinary problems in a unified manner. New topics include supercritical fluid dynamics, boiling near the critical point, stress–diffusion coupling in polymers, patterns and heterogeneities in gels, and mesoscopic dynamics at structural phase transitions in solids. In the final chapter, theoretical and experimental approaches to shear flow problems in fluids are reviewed.

Phase Transition Dynamics provides a comprehensive treatment of the study of phase transitions. Building on the statics of phase transitions, covered in many introductory textbooks, it will be essential reading for researchers and advanced graduate students in physics, chemistry, metallurgy and polymer science.

AKIRA ONUKI obtained his PhD from the University of Tokyo. Since 1983 he has held a position at Kyoto University, taking up his current professorship in 1991. He has made important contributions to the study of phase transition dynamics in both fluid and solid systems.

Phase Transition Dynamics

AKIRA ONUKI

Kyoto University



> PUBLISHED BY THE PRESS SYNDICATE OF THE UNIVERSITY OF CAMBRIDGE The Pitt Building, Trumpington Street, Cambridge, United Kingdom

CAMBRIDGE UNIVERSITY PRESS The Edinburgh Building, Cambridge CB2 2RU, UK 40 West 20th Street, New York, NY 10011-4211, USA 477 Williamstown Road, Port Melbourne, VIC 3207, Australia Ruiz de Alarcón 13, 28014, Madrid, Spain Dock House, The Waterfront, Cape Town 8001, South Africa

http://www.cambridge.org

© A. Onuki 2002

This book is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2002

Printed in the United Kingdom at the University Press, Cambridge

Typeface Times 10/13pt. System LATEX 2_{ε} [DBD]

A catalogue record of this book is available from the British Library

Library of Congress Cataloguing in Publication data

Onuki, Akira. Phase transition dynamics / Akira Onuki p. cm. Includes bibliographical references and index. ISBN 0 521 57293 2

1. Phase transformations (Statistical physics). 2. Condensed matter. I. Title

> QC175.16.P5 O58 2002 530.4'14–dc21 2001037340

ISBN 0521572932 hardback

Contents

Pre	face	<i>page</i> ix
	Part one: Statics	1
1	Spin systems and fluids	3
	1.1 Spin models	3
	1.2 One-component fluids	10
	1.3 Binary fluid mixtures	23
	Appendix 1A Correlations with the stress tensor	30
	References	32
2	Critical phenomena and scaling	34
	2.1 General aspects	34
	2.2 Critical phenomena in one-component fluids	45
	2.3 Critical phenomena in binary fluid mixtures	53
	2.4 ⁴ He near the superfluid transition	66
	Appendix 2A Calculation in non-azeotropic cases	74
	References	75
3	Mean field theories	78
	3.1 Landau theory	78
	3.2 Tricritical behavior	84
	3.3 Bragg–Williams approximation	90
	3.4 van der Waals theory	99
	3.5 Mean field theories for polymers and gels	104
	Appendix 3A Finite-strain theory	119
	References	122
4	Advanced theories in statics	124
	4.1 Ginzburg–Landau–Wilson free energy	124
	4.2 Mapping onto fluids	133
	4.3 Static renormalization group theory	144
	4.4 Two-phase coexistence and surface tension	162
	4.5 Vortices in systems with a complex order parameter	173
	Appendix 4A Calculation of the critical exponent η	178
	Appendix 4B Random phase approximation for polymers	179

vi	Contents	
	 Appendix 4C Renormalization group equations for <i>n</i>-component systems Appendix 4D Calculation of a free-energy correction Appendix 4E Calculation of the structure factors Appendix 4F Specific heat in two-phase coexistence References 	180 181 182 183 184
	Part two: Dynamic models and dynamics in fluids and polymers	189
5	 Dynamic models 5.1 Langevin equation for a single particle 5.2 Nonlinear Langevin equations with many variables 5.3 Simple time-dependent Ginzburg–Landau models 5.4 Linear response Appendix 5A Derivation of the Fokker–Planck equation Appendix 5B Projection operator method Appendix 5C Time reversal symmetry in equilibrium time-correlation functions Appendix 5D Renormalization group calculation in purely dissipative dynamics Appendix 5E Microscopic expressions for the stress tensor and energy current References 	 191 191 198 203 211 217 217 222 222 223 224
6	Dynamics in fluids6.1Hydrodynamic interaction in near-critical fluids6.2Critical dynamics in one-component fluids6.3Piston effect6.4Supercritical fluid hydrodynamics6.5Critical dynamics in binary fluid mixtures6.6Critical dynamics near the superfluid transition6.7 ⁴ He near the superfluid transition in heat flowAppendix 6ADerivation of the reversible stress tensorAppendix 6BCalculation in the mode coupling theoryAppendix 6CSteady-state distribution in heat flowAppendix 6DCalculation of the piston effectReferencesEffect	227 227 237 252 265 271 281 298 307 308 309 310 311
7	 Dynamics in polymers and gels 7.1 Viscoelastic binary mixtures 7.2 Dynamics in gels 7.3 Heterogeneities in the network structure Appendix 7A Single-chain dynamics in a polymer melt Appendix 7B Two-fluid dynamics of polymer blends Appendix 7C Calculation of the time-correlation function Appendix 7D Stress tensor in polymer solutions 	317 317 335 351 359 360 362 362

	Contents	vi
	Appendix 7E Elimination of the transverse degrees of freedom	363
	Appendix 7F Calculation for weakly charged polymers	365
	Appendix 7G Surface modes of a uniaxial gel	366
	References	366
	Part three: Dynamics of phase changes	371
8	Phase ordering and defect dynamics	373
	8.1 Phase ordering in nonconserved systems	373
	8.2 Interface dynamics in nonconserved systems	389
	8.3 Spinodal decomposition in conserved systems	400
	8.4 Interface dynamics in conserved systems	407
	8.5 Hydrodynamic interaction in fluids	421
	8.6 Spinodal decomposition and boiling in one-component fluids	432
	8.7 Adiabatic spinodal decomposition	437
	8.8 Periodic spinodal decomposition	44(
	8.9 Viscoelastic spinodal decomposition in polymers and gels	444
	8.10 Vortex motion and mutual friction	45.
	Appendix 8A Generalizations and variations of the Porod law	46
	Appendix 8B The pair correlation function in the nonconserved case	47.
	Appendix 8C The Kawasaki-Yalabik-Gunton theory applied to periodic	
	quench	47
	Appendix 8D The structure factor tail for $n = 2$	47:
	Appendix 8E Differential geometry	47
	Appendix 8F Calculation in the Langer–Bar-on–Miller theory	47
	Appendix 8G The Stefan problem for a sphere and a circle	47
	Appendix 8H The velocity and pressure close to the interface	47
	Appendix 8I Calculation of vortex motion	48
	References	482
9	Nucleation	48
	9.1 Droplet evolution equation	48
	9.2 Birth of droplets	49
	9.3 Growth of droplets	50
	9.4 Nucleation in one-component fluids	51
	9.5 Nucleation at very low temperatures	53
	9.6 Viscoelastic nucleation in polymers	53
	9.7 Intrinsic critical velocity in superfluid helium	53
	Appendix 9A Relaxation to the steady droplet distribution	54
	Appendix 9B The nucleation rate near the critical point	54
	Appendix 9C The asymptotic scaling functions in droplet growth	54
	Appendix 9D Moving domains in the dissipative regime	540
	Appendix 9E Piston effect in the presence of growing droplets	547

viii	Contents	
	Appendix 9F Calculation of the quantum decay rate References	547 548
10	Phase transition dynamics in solids	552
	10.1 Phase separation in isotropic elastic theory	556
	10.2 Phase separation in cubic solids	577
	10.3 Order–disorder and improper martensitic phase transitions	584
	10.4 Proper martensitic transitions	593
	10.5 Macroscopic instability	615
	10.6 Surface instability	622
	Appendix 10A Elimination of the elastic field	625
	Appendix 10B Elastic deformation around an ellipsoidal domain	629
	Appendix 10C Analysis of the Jahn–Teller coupling	630
	Appendix 10D Nonlocal interaction in 2D elastic theory	631
	Appendix 10E Macroscopic modes of a sphere	632
	Appendix 10F Surface modes on a planar surface	635
	References	635
11	Phase transitions of fluids in shear flow	641
	11.1 Near-critical fluids in shear	642
	11.2 Shear-induced phase separation	668
	11.3 Complex fluids at phase transitions in shear flow	684
	11.4 Supercooled liquids in shear flow	686
	Appendix 11.A Correlation functions in velocity gradient	700
	References	701
Inde	2x	710

Preface

This book aims to elucidate the current status of research in phase transition dynamics. Because the topics treated are very wide, a unified phenomenological time-dependent Ginzburg–Landau approach is used, and applied to dynamics near the critical point. Into the simple Ginzburg–Landau theory for a certain order parameter, we introduce a new property or situation such as elasticity in solids, viscoelasticity in polymers, shear flow in fluids, or heat flow in ⁴He near the superfluid transition. By doing so, we encounter a rich class of problems on mesoscopic spatial scales. A merit of this approach is that we can understand such diverse problems in depth using universal concepts.

The first four chapters (Part one) deal with static situations, mainly of critical phenomena, and introduce some new results that would stand by themselves. However, the main purpose of Part one is to present the definitions of many fundamental quantities and introduce various phase transitions. So it should be read before Parts two and three which deal with dynamic situations. Chapter 5 is also introductory, reviewing fundamental dynamic theories, the scheme of Langevin equations and the linear response theory. Chapter 6 treats critical dynamics in (i) classical fluids near the gas-liquid and consolute critical points and (ii) ⁴He near the superfluid transition. Chapter 7 focuses on rather special problems in complex fluids: (i) effects of viscoelasticity on composition fluctuations in polymer systems; and (ii) volume phase transitions and heterogeneity effects in gels. Chapters 8 and 9 (in Part three) constitute the main part of this book, and consider the kinetics of phase ordering, spinodal decomposition, and nucleation. Motions of interfaces and vortices are examined in the Ginzburg-Landau models. Chapter 10 focuses on dynamics in solids, including phase separation, order-disorder and martensitic transitions, shape instability in hydrogen-metal systems, and surface instability in metal films. These problems have hitherto been very inadequately studied and most papers are difficult to understand for those outside the field, so it was important to write this chapter in a coherent fashion, though it has turned out to be a most difficult task. I believe that many interesting dynamical problems remain virtually unexplored in solids, because such phenomena have been examined either too microscopically in solid-state physics without giving due respect to long-range elastic effects or with technologically-oriented objectives in engineering. Chapter 11 is on shear flow problems in fluids, a topic on which a great number of theoretical and experimental papers appeared in the 1980s and 1990s. This book thus covers a wide range of phase transition dynamics. Of course, many important problems had to be omitted.

I have benefited from discussions with many people working in the fields of lowtemperature physics, statistical physics, polymer science, and metallurgy. Particularly

х

Preface

useful suggestions were given by H. Meyer, Y. Oono, K. Kawasaki, T. Ohta, M. Doi, T. Hashimoto, H. Tanaka, M. Shibayama, T. Miyazaki, T. Koyama, and Y. Yamada. Thanks are due to R. Yamamoto, K. Kanemitsu, and A. Furukawa for drawing some of the figures. It is with deep sadness that I record the deaths of T. Tanaka and K. Hamano. It is a great pleasure to be able to acknowledge their memorable contributions to Chapters 7 and 11, respectively. Finally, I apologize to my students, colleagues, and family, for any difficulty they may have experienced because I have been so busy with this extremely time-consuming undertaking.

Akira Onuki Kyoto, Japan