## Contents

Preface and Acknowledgments	xi
1. Introduction: Metastable Liquids in Nature	1
and Technology	1
1.1 Introduction	2
1.1.1 Definitions	2
1.1.2 Two Experiments: Superheated and Supercooled	_
Water in the Laboratory	5
1.2 Metastable Liquids in Nature	9
1.2.1 Life at Low Temperatures	9
1.2.2 Proteins at Low Temperatures	14
1.2.3 The Ascent of Sap in Plants	20 25
1.2.4 Mineral Inclusions	23 27
1.2.5 Clouds	32
1.3 Metastable Liquids in Technology 1.3.1 Storage of Proteins and Cells by Supercooling	32
1.3.2 Some Uses of Liquids under Tension	34
1.3.3 Vapor Explosions	39
1.3.4 Kinetic Inhibition of Natural Gas Clathrate Hydrates	47
References	51
2. Thermodynamics	63
2.1 Phenomenological Approach: Stability Criteria	64
2.2 Phenomenological Approach: Stability of Pure Fluids	66
2.2.1 Superheated Liquids	68
2.2.2 The Spinodal Envelope	71
2.2.3 The van der Waals Fluid	71
2.2.4 Pseudocritical and Critical Exponents	72
2.2.5 Stability Limit Predictions with Equations of State	81
2.2.6 Continuity and Divergences in Superheated Liquids	83
2.2.7 The "Pseudospinodal"	90
2.2.8 Liquids That Expand When Cooled: The Stability Limit Conjecture	93

	<ul><li>2.2.9 Metastable Phase Equilibrium</li><li>2.3 Phenomenological Approach: Stability of Fluid Mixtures</li></ul>	100 105
	2.3.1 Binary Mixtures	105
	2.3.2 Multicomponent Mixtures	115
	2.4 Critique of the Phenomenological Approach:	
	Metastability and Statistical Mechanics	121
	2.5 Stability of Liquids with Respect to Crystalline Solids	133
	References	136
3.	Kinetics	147
	3.1 Homogeneous Nucleation	148
	3.1.1 Classical Nucleation Theory	148
	3.1.2 Energetics of Embryo Formation:	
	Rigorous Approaches	159
	3.1.3 Kinetic Nucleation Theories	171
	3.1.4 Homogeneous Nucleation in Superheated Liquids	176
	3.1.5 Homogeneous Nucleation in Supercooled Liquids	187
	3.1.6 The Approach to Steady State	196
	3.2 Spinodal Decomposition	199
	3.3 The Transition From Nucleation to	
	Spinodal Decomposition	209
	3.4 Heterogeneous Nucleation	216
	References	223
4.	Supercooled Liquids	235
	4.1 Crystallization and Vitrification	236
	4.2 Elementary Phenomenology of Vitrification	2.11
	upon Supercooling	241
	4.3 Thermodynamic Viewpoint of the Glass Transition	246
	4.3.1 Kauzmann's Paradox	247
	4.3.2 Cooperative Relaxations and the Entropy Viewpoin	
	4.3.3 Free Volume Theory	272
	4.4 Dynamic Viewpoint of the Glass Transition:	282
	Mode Coupling	282 301
	<ul><li>4.5 Strong and Fragile Liquids</li><li>4.6 Supercooled and Glassy Water</li></ul>	301
		305
	4.6.1 Experiments 4.6.2 Interpretation	300
	4.6.3 Glassy Water	311
	4.0.5 Glassy Water 4.7 Computer Simulation of Supercooled Liquids	330
	References	345
		545

CONTENTS	ix
5. Outlook	363,
APPENDIX 1: Stability of Fluids: Thermodynamic and	
Mathematical Proofs	367
APPENDIXI 2: Thermodynamics of Fluid Interfaces	377
APPENDIX 3: Definitions of Microscopic and Statistical Quantities	389
INDEX	397