

Contents

1 Thermodynamics and Statistical Mechanics of Phase Transitions	1
1.1 What is a Phase Transition?	1
1.2 Thermodynamic Description of Phase Transitions	4
1.2.1 Stability and Transition – Gibbs–Duhem Criterion.....	4
1.2.2 Phase Diagrams	7
1.2.3 Thermodynamic Classification of Phase Transitions ...	14
1.3 General Principles of Methods of Investigating Phase Transitions	17
1.3.1 Calculation of Thermodynamic Potentials and Quantities	18
1.3.2 Equation of State	21
1.3.3 Dynamic Aspects – Fluctuations	22
1.4 The Broad Categories of Phase Transitions	25
1.4.1 Transitions with a Change in Structure	25
1.4.2 Transitions with No Change in Structure	28
1.4.3 Non-Equilibrium Transitions	28
1.5 The Major Experimental Methods for Investigation of Phase Transitions	29
1.6 The Broad Categories of Applications of Phase Transitions ..	31
1.7 Historical Aspect: From the Ceramics of Antiquity to Nanotechnologies	32
Problems	34
2 Dynamics of Phase Transitions	37
2.1 A Large Variety of Mechanisms	37
2.2 Nucleation	38
2.2.1 The Diffusion Phenomenon – Fick’s Law	38
2.2.2 Diffusion Coefficient and Activation Energy.....	39
2.2.3 Nucleation of a New Phase	40
2.2.4 Nucleation Rate	46
2.2.5 Global Phase Transformation – Avrami Model	51
2.3 Spinodal Decomposition	56
2.3.1 Thermodynamics of Spinodal Decomposition.....	57

X Contents

2.3.2	Experimental Demonstration – Limitation of the Model	62
2.4	Structural transition	64
2.4.1	Dynamics of a Structural Transition – The Soft Mode .	65
2.4.2	Martensitic Transformation	66
2.5	Fractals – Percolation	67
2.5.1	Fractal Structures	67
2.5.2	Percolation and Gelation	72
2.6	Dynamics of Phase Transitions and Properties of Materials ..	75
	Problems	77
3	Phase Transitions in Liquids and Solids:	
	Solidification and Melting	79
3.1	Ubiquitous Phenomena	79
3.2	Characterization of the Phenomena	80
3.2.1	Thermodynamic Characterization	80
3.2.2	Microscopic Approach	82
3.2.3	Delays in the Transition: Supercooling–Superheating ..	84
3.2.4	Methods of Observation and Measurement	87
3.3	Melting	90
3.3.1	The Lindemann Model	90
3.3.2	The Role of Defects	92
3.3.3	Melting and Surface of Materials	94
3.4	Solidification	95
3.4.1	Theoretical Approach to Crystallization with Intermolecular Potentials	97
3.4.2	Case of Colloids	104
3.4.3	Crystallization and Melting of Polymers	105
3.5	Crystallization, Melting, and Interface	110
3.5.1	Surface Melting	111
3.5.2	Size Effect on Small Particles	113
3.5.3	The Special Case of Ice	113
3.6	Very Numerous Applications	116
3.6.1	Melting – Solidification in Metallurgy	116
3.6.2	Molding of Polymers	118
3.6.3	Production of Sintered Ceramics	119
	Problems	121
4	Phase Transitions in Fluids	123
4.1	The Approach Using Equations of State	123
4.2	The Liquid–Gas Transition in Simple Liquids	125
4.2.1	Van der Waals Equation of State	125
4.2.2	The Law of Corresponding States	126
4.2.3	Behavior Near the Critical Point	128
4.3	Thermodynamic Conditions of Equilibrium	130
4.3.1	Liquid–Gas Equilibrium	130

4.3.2	Maxwell's Rule	132
4.3.3	Clausius–Clapeyron and Ehrenfest Equations	132
4.4	Main Classes of Equations of State for Fluids	134
4.4.1	General Principles	134
4.4.2	One-Component Fluids	134
4.4.3	Variants of the van der Waals Equation	135
4.5	Metastable States: Undercooling and Overheating	137
4.5.1	Returning to Metastability	137
4.5.2	Formation of Drops and Bubbles	138
4.6	Simulation of Phase Transitions	139
4.6.1	Principles	139
4.6.2	Molecular Dynamics	139
4.6.3	Monte Carlo Method	141
4.7	Binary Mixture of Two Components	143
4.7.1	Conditions of Phase Equilibrium in a Binary Mixture .	143
4.7.2	Systems in the Vicinity of a Critical Point	145
4.7.3	Equation of State of Mixtures	146
4.7.4	Mixtures of Polymers or Linear Molecules	152
4.7.5	Binary Mixtures far from the Critical Point	153
4.7.6	Supercritical Unmixing	156
4.7.7	Tricritical Points	157
	Problems	161
5	The Glass Transition	163
5.1	Glass Formation	163
5.2	The Glass Transition	166
5.2.1	Thermodynamic Characteristics	166
5.2.2	Behavior of the Viscosity	169
5.2.3	Relaxation and Other Time Behaviors	171
5.3	The Structure of Glasses	171
5.3.1	Mode-Coupling Theory	174
5.3.2	Industrial Applications	181
5.3.3	Models for Biological Systems	182
	Problems	183
6	Gelation and Transitions in Biopolymers	185
6.1	The Gel State and Gelation	185
6.1.1	Characterization of a Gel	185
6.1.2	The Different Types of Gels	186
6.2	Properties of Gels	188
6.2.1	Thermal Properties	188
6.2.2	Mechanical Properties	190
6.3	A Model For Gelation: Percolation	192
6.3.1	The Percolation Model	193
6.4	Biopolymers Gels	196

XII Contents

6.4.1	An Important Gel: Gelatin	196
6.4.2	Polysaccharide Gels.....	199
6.4.3	Modeling of the Coil \leftrightarrow Helix Transition	200
6.4.4	Statistical Model	201
6.5	Main Applications of Gels and Gelation	206
	Problems	208
7	Transitions and Collective Phenomena in Solids. New Properties	211
7.1	Transitions with Common Characteristics	211
7.2	The Order–Disorder Transition in Alloys	213
7.3	Magnetism	217
7.3.1	Characterization of Magnetic States	217
7.3.2	The Molecular Field Model	218
7.3.3	Bethe Method	221
7.3.4	Experimental Results	225
7.4	Ferroelectricity	226
7.4.1	Characteristics	226
7.4.2	The Broad Categories of Ferroelectrics	227
7.4.3	Theoretical Models – the Landau Model	229
7.5	Superconductivity	232
7.5.1	A Complex Phenomenon	232
7.5.2	Theoretical Models	234
7.6	Universality of Critical Phenomena	237
7.6.1	Critical Exponents and Scaling Laws.....	237
7.6.2	Renormalization Group Theory	239
7.7	Technological Applications.....	241
	Problems	243
8	Collective Phenomena in Liquids: Liquid Crystals and Superfluidity	247
8.1	Liquid Crystals	247
8.1.1	Partially Ordered Liquid Phases.....	247
8.1.2	Definition of Order in the Liquid Crystal State	248
8.1.3	Classification of Mesomorphic Phases	249
8.1.4	The Nematic Phase and Its Properties	255
8.1.5	The Many Applications of Liquid Crystals	282
8.1.6	Mesomorphic Phases in Biology	285
8.2	Superfluidity of Helium	286
8.2.1	Helium 4	286
8.2.2	Superfluidity in Helium 3.....	296
	Problems	298

9 Microstructures, Nanostructures and Phase Transitions	299
9.1 The Importance of the Microscopic Approach	299
9.2 Microstructures in Solids	300
9.2.1 Solidification and Formation of Microstructures	300
9.2.2 A Typical Example: The Martensitic Transformation ..	303
9.2.3 Singular Phases: The Quasicrystals	305
9.2.4 The Special Case of Sintering in Ceramics	306
9.2.5 Microstructures in Ferromagnetic, Ferroelectric, and Superconducting Phases	310
9.3 Microstructures in Fluid Phases	318
9.3.1 Microemulsions	318
9.3.2 Colloids	320
9.4 Microstructure, Nanostructures, and Their Implications in Materials Technology	323
Problems	325
10 Transitions in Thin Films	327
10.1 Monolayers at the Air–Water Interface	327
10.1.1 The Role of Surfactants	327
10.1.2 Examples of Molecules Forming Monolayers	328
10.1.3 Preparation and Thermodynamics Study of Monolayers	329
10.1.4 Phase Diagram of a Monolayer	330
10.2 Monolayer on the Surface of a Solid	335
11 Phase Transitions under Extreme Conditions and in Large Natural and Technical Systems	337
11.1 Phase Transitions under Extreme Conditions	337
11.1.1 Experimental Methods	337
11.1.2 Equations of State and Phase Transitions under Extreme Conditions	339
11.1.3 Geomaterials	343
11.1.4 The Plasma State	344
11.1.5 Bose–Einstein Condensates at Extremely Low Temperature	345
11.2 The Role of Phase Transitions in the Ocean–Atmosphere System	346
11.2.1 Stability of an Atmosphere Saturated with Water Vapor	347
11.2.2 Thermodynamic Behavior of Humid Air	351
11.2.3 Formation of Ice in the Atmosphere – Melting of Ice and Climate	354
11.3 Phase Transitions in Technical Systems	355
11.3.1 Vaporization in Heat Engines	356

XIV Contents

11.3.2 The Cavitation Phenomenon	358
11.3.3 Boiling Regimes	359
11.3.4 Phase Transitions and Energy Storage	362
Problems	363
A. Conditions for Phase Equilibrium.....	379
B. Percus–Yevick Equation	381
C. Renormalization Group Theory	385
Bibliography	387
Index	393